SANDSTONE ACIDIZING USING CHELATING AGENTS

BY

AHMED ABDULAZEEM AHMED HAMZA

A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

PETROLEUM ENGINEERING

May 2016

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

This thesis, written by **AHMED ABDULAZEEM AHMED HAMZA** under the direction his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN PETROLEUM ENGINEERING**

Dr. Mohamed A. Mahmoud
(Advisor)

Dr. Abdullah S. Sultan
Department Chairman

Dr. Abdullah S. Sultan
(Member)

Dr. Salam A. Zummo
Dean of Graduate Studies

Dr. Ibnelwaleed A. Hussein
(Member)

5/5/16
Date

This work is dedicated to my lovely family.

ACKNOWLEDGMENTS

I would like to thank King Fahd University of Petroleum & Minerals for the Scholarship to study the master degree.

I would like to express my sincere gratitude to my advisor Dr. Mohamed A. Mahmoud for his patience, assistance and guidance throughout this research. His guidance helped me in all the time of research and writing of this thesis. I also want to extend my appreciation to Prof. Ibnelwaleed A. Hussein and Dr. Abdullah S. Sultan for devoting their valuable time to review the research and evaluate its results.

I wish to express my thanks to staff of petroleum engineering department and Center of Petroleum and Minerals for their help during the experiments. I thank my friends for the valuable discussions and all the fun we have had during the master program.

Last but not the least, I would like to thank my family for supporting me throughout my life in general.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

EDTA	:	Ethylene diaminete tra acetic acid
HEDTA	:	Hydroxy ethylene diamine triacetic acid
DTPA	:	Diethylene triamine Penta acetic acid
E20	:	EDTA 20 wt. %
E20C3	:	EDTA 20 wt. % / potassium carbonate 3 wt. %
D20	:	DTPA 20 wt. %
D20C3	:	DTPA 20 wt. % / potassium carbonate 3 wt. %
H20	:	HEDTA 20 wt. %
H20C3	:	HEDTA 20 wt. % / potassium carbonate 3 wt. %
DI	:	Deionized water
Sea	:	Seawater
BN	:	Bandera Gray sandstone.
BR	:	Gray Berea sandstone.
$K_{initial}$	:	Initial permeability before treatment, mD.
K_{final}	:	Final permeability after treatment, mD.

$Ø_i$	:	Initial porosity, %
L	:	Length of the core, inch.
P-waves	:	Primary waves
S-waves	:	Secondary (shear) waves
E	:	Young's modulus, GPa.
$\boldsymbol{\rho}$	:	Rock density, gm/cm^3
$\boldsymbol{v}$	:	Poisson's ratio
G	:	Shear modulus v_s
K	:	Bulk modulus
$\boldsymbol{v_p}$	:	Velocity of primary wave, m/s.
$\boldsymbol{v_s}$	:	Velocity of shear wave, m/s.
PVs	:	Pore volumes.

ABSTRACT

Full Name :Ahmed Abdulazeem Ahmed Hamza

Thesis Title :Sandstone Acidizing Using Chelating Agents

Major Field :Petroleum Engineering

Date of Degree :May 2016

Chelating agents were used recently to stimulate sandstone formations. The objective of this study is to introduce Diethylene tri-amine penta-acetic acid (DTPA) diluted using deionized water and seawater combined with potassium carbonate to stimulate sandstone reservoirs.

Solubility tests were conducted to determine the optimum concentration of the chelating agent and potassium carbonate catalyst. Solutions of Ethylene diamine tetra-acetic acid (EDTA), Hydroxyl ethylene diamine tri-acetic acid (HEDTA) and DTPA at high pH combined with potassium carbonate were used. Moreover, the effect of temperature on the solubility was examined. Core flooding experiments were conducted to evaluate the efficiency of the new formulated fluids as a standalone stimulation fluid for Berea and Bandera sandstone formations. The effects of injection rate, temperature, injected volume of acid and core length were studied. Furthermore, acoustic measurements and computed tomography (CT) scan were used to address the impact of the new formulated fluids on the rock integrity and mechanical properties of the sandstone cores.

The results of solubility tests showed that the optimum concentration of chelating agents (EDTA, HEDTA and DTPA) in the new formulated fluids is 20 wt. % and the ratio of

potassium carbonate catalyst is 3 wt. % at pH of 11. No precipitations were noticed when deionized water and seawater were used to dilute the acids. The highest solubility was recorded for Bandera samples treated using DTPA at 150^{o}F and it was around 23 %.

Berea and Bandera cores with length of 2 - 6 inches were flooded by EDTA and DTPA acids at pH of 11 using 6 pore volumes. The permeability ratio improved by 39 % for Berea after adding the 3 wt. % of catalyst to 20 wt. % DTPA diluted using deionized water at pH of 11 and the injection rate was 5 cm^3/min at temperature 250^{o}F. For Bandera cores, diluting the acids with seawater showed 40 % enhancement in permeability ratio. Decreasing the injection rate increased the permeability ratio to more than double for Berea and 70 % for Bandera using DTPA seawater base with 3 wt. % of the catalyst. The new formulated fluid worked better at 250^{o}F thus decreasing the temperature to 150^{o}F reduced its efficiency. Using long cores (6 inches) showed the performance of the new formulation better than 2 inches cores.

Rock mechanical results showed the effect of injected pore volume of the acid on the rock integrity. Bandera cores acidized with 20 wt. % DTPA combined with 3 wt.% potassium carbonate diluted using seawater showed the largest decrease in Young's modulus value as well as highest permeability enhancement after injecting 10 pore volumes. Berea samples showed insignificant change in elastic moduli values. According to shear modulus to bulk compressibility ratio sand production is not expected to happen at this conditions.

ملخص الرسالة

الاسم الكامل : أحمد عبد العظيم أحمد حمزة

عنوان الرسالة : حقن الطبقات الرملية باستخدام المركبات المخلبية

التخصص : هندسة النفط

تاريخ الدرجة العلمية : مايو 2016

استخدمت المركبات المخلبية حديثا في عملية حقن الأحماض لتحسين الطبقات الرملية. الغرض من هذا البحث تقديم حمض ثنائي الإيثالين ثلاثي أمين خماسي حمض الخليك (DTPA) المخفف باستخدام الماء الخالي من الأيونات وماء البحر مدمج مع كاربونات البوتاسيوم لتحسين المكامن الرملية.

استخدمت اختبارات الذوبانية لتحديد نسبة التركيب المثالي للأحماض المركبة من حيث التركيز الوزني للمركبات المخلبية ، نسبة التركيز الوزني للعامل الحفاز في المركبات المخلبية. استخدم حمض إيثايلين ثنائي أمين رباعي حمض الخليك (EDTA) و هيدروكسي إيثايلين ثنائي أمين ثلاثي حمض الخليك (HEDTA) و ثنائي الإيثالين ثلاثي أمين خماسي حمض الخليك (DTPA) عند درجة حموضة عالية مع اضافة كربونات البوتاسيوم. بالإضافة إلى ذلك ، تم تحديد أثر درجة الحرارة على نسبة الذوبانية. اجريت تجارب الحقن لتحديد فعالية المركبات الحمضية الجديدة كموائع قائمة بذاتها لتحسين صخري بيريا و باندیرا الرمليين. تم دراسة تأثير معدل الحقن، درجة الحرارة، الحجم الحمض الذي تم حقنه و طول العينة الاسطوانية الصخرية. علاوة على ذلك، استخدمت القياسات الصوتية لتحديد أثر الحمض على تماسك الصخر و الخواص الميكانيكية.

اوضحت نتائج اختبارات الذوبانية أن تركيز المركبات المخلبية المثالي (EDTA, HEDTA & DTPA) في المركبات الحمضية الجديدة هو 20 % نسبة وزنية و النسبة المئوية للعامل الحافز كربونات البوتاسيوم هو 3 % نسبة وزنية عند نسبة حموضة 11. لم يتم ملاحظة أي رواسب عند استخدام الماء الخالي من الأيونات أو ماء البحر. سجلت

أعلى نسبة ذوبانية لعينات صخر باندیرا الرملي بعد معالجتها باستخدام حمض دي تي بي اي عند درجة حرارة 150 درجة فهرنهايت وكانت حوالي 23 %.

اجريت اختبارات الحقن على عينات اسطوانية من صخري بيريا و باندیرا بطول 2 إلى 6 بوصات باستخدام حمضي إي دي تي اي و دي تي بي اي بمقياس حموضة 11 و استخدام 6 احجام مسامية. تحسنت نسبة النفاذية بنسبة 39 % لصخر بيرييا بعد إضافة 3 % نسبة وزنية من العامل الحفاز إلى 20 % من حمض دي تي بي اي الذي تم تخفيفه باستخدام الماء الخالي من أيونات عند مقياس حموضة 11 و معدل حقن 5 سم^3/دقيقة عند درجة حرارة 150 درجة فهرنهايت.عند تخفيف الحمض باستخدام ماء البحر كانت نسبة تحسين النفاذية 40 % لحمض دي تي بي اي الذي تركيزه 20 % نسبة وزنية. عند تقليل معدل الحقن زادت نسبة النفاذية إلى أكثر من الضعف لصخر بيرييا و 70 % لصخر باندیرا باستخدام حمض دي تي بي اي المخفف بماء البحر مع اضافة 3 % نسبة وزنية من العامل الحافز. الأحماض المركبة الجديدة تعمل بصورة جيدة عند درجة حرارة 250 درجة فهرنهايت لذلك عند تخفيض درجة الحرارة إلى 150 درجة فهرنهايت تقل فعاليتها. تم توضيح أداء المركبات الجديدة باستخدام عينات صخرية اسطوانية طويلة (6 بوصات) بصورة أفضل من العينات الاسطوانية بطول بوصتين.

أوضحت نتائج الاختبارات الصوتية للخواص الميكانيكية للصخور تأثير الحجم المسامي الذي تم حقنه من الحمض على تماسك الصخر. نقص معامل يونغ عند زيادة الحجم المسامي الذي تم حقنه تشير إلى نجاح المعالجة. تم الحصول على أعلى نسبة نقص في معامل يونغ عند حقن عينات باندیرا الاسطوانية بحمض دي تي بي اي مع اضافة 3 % من كربونات البوتاسيوم و تخفيف المحلول بماء البحر و أعلى نسبة تحسن للنفاذية بعد حقن 10 أحجام مسامية. لم يتم ملاحظة تغيير ذو أهمية في قيم معاملات المرونة لعينات بيرييا الاسطوانية. بناء على قيم نسبة معامل القص لمعامل الانضغاطية الكلي لا يتوقع ان يتم انتاج رمل في نفس ظروف تجارب الحقن.

CHAPTER 1

INTRODUCTION

Acidizing is a process to enhance the productivity of the well by dissolving restriction flow materials. Sandstone formations are stimulated using acids to reduce the damage caused during drilling or completion of the well to the production zone. Sandstone acidizing is usually carried out by matrix acidizing in which the injection pressure is less than the formation fracturing pressure. This process can be considered as damage removal so fractured or undamaged wells are not candidates of it.

Sandstone formations have many minerals include dolomite, calcite, quartz, feldspar and clays. These minerals can be either from invasion of drilling and/or completion fluids, cementing or from materials that consist rock formations. **Table 1** illustrates minerals in different types of sandstones and clay content.

1.1 Clay Minerals

Clay is a tiny (size less than 0.005 mm) plat-shaped materials that can be found in sedimentary formations as packages of crystalline minerals described as hydrous aluminum silicates occupying a large fraction of sedimentary rock. **Figure 1** shows the composition of typical sandstone. Clay can be encountered in sandstones and cause many problems during the acidizing process. It is essential to determine the mineralogy and chemical composition of the clay because these factors control the reaction between the

clay and the acid, swelling, solubility of minerals and type and amount of precipitates. Sensitivity of clay minerals to specific acid depends on the surface area (Civan 2007). The clay spreading and its type have major impact on the ion exchange capacity of the sandstone formation and the surface area of the rock (Crocker et al, 1983).

Table 1 Sandstone Types and Percentage of Clays Content (Mahmoud et al., 2015).

Mineral	Berea	Bandera	Kentucky	Scioto
Quartz	86	57	66	70
Dolomite	1	16	--	--
Calcite	2	--	--	--
Feldspar	3	--	2	2
Kaolinite	5	3	Trace	Trace
Illite	1	10	14	18
Chlorite	2	1	--	4
Plagioclase	--	12	17	5

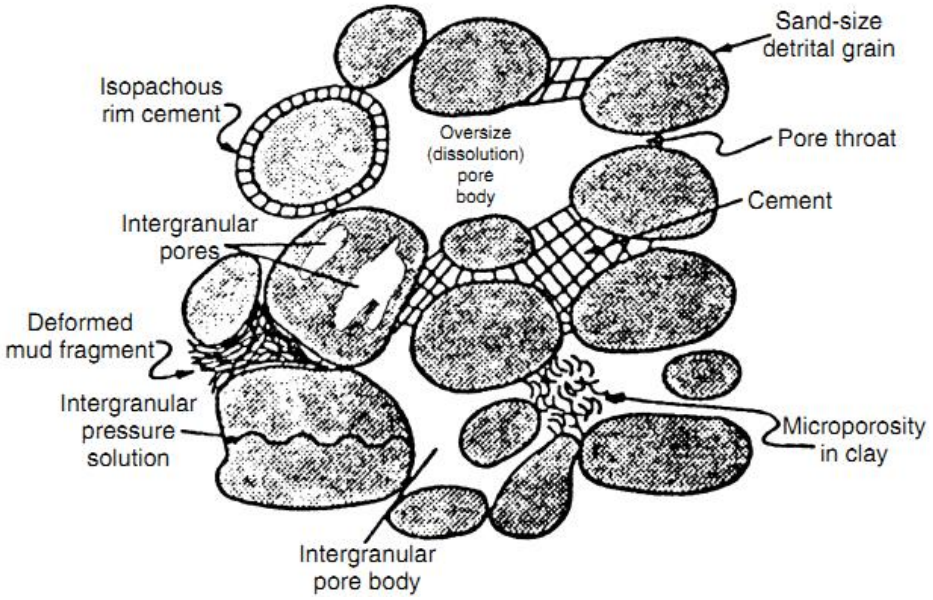


Figure 1 Description of Contents of Typical Sandstone (Civan 2007).

Clay minerals are commonly classified based on the number and type of layers. The main groups of clay minerals are kaolinite, smectite (montmorillonite), illite and chlorite. Moreover, a mixed-layer clay minerals formed from these groups can be confronted. Civan (2007) described properties and damage processes of the clay groups as following:

1.1.1 Kaolinite ($Al_2Si_2O_5(OH)_4$): is a layered silicate mineral with one tetrahedral sheet linked to one octahedral sheet of alumina through oxygen atoms (**Figure 2**). It has two-layer structure and can exchange potassium cations. It is mainly non-swelling clay but has the ability to break apart and migrate causing severe damage. Damage from migrated kaolinite fines is located in the near wellbore area. Kaolinite can adsorb some water; the adsorbed water is held tightly to the clay's surface. Moreover, it has low cation-exchange capacity.

1.1.2 Smectite (Montmorillonite) $[(0.5Ca,Na)_{0.7}(Al,Mg,Fe)_4[Si,Al)_8O_{20}].nH_{2O}]$ has three-layer structure (**Figure 3**), large base exchange capacity of 90 to 150 meq/l00g and able to adsorb Na^+. These properties are leading to a high degree of swelling and dispersion. Water causes smectite swelling and its volume can increase up to 600% which will might cause significant reduction in permeability.

1.1.3 Illite ($K_{1-1.5}Al_4[Si_{7-6.5}Al_{1-1.5}O_{20}](OH)_4$) is interlayered (**Figure 4**), so it combines the properties of both the dispersible and swellable clays. It is very rich with potassium cations and when these cations released the illite will expand.

1.1.4 Chlorite $[(Mg, Al, Fe)_{12}[Si, Al)_8O_{20}](OH)_{16}]$ is very sensitive to acids and oxygenated water. It causes the precipitation of $Fe(OH)_3$. Chlorite has huge surface area approximately 100 m^2/gm.

1.1.5 Mixed layer has wide range surface area 100-700 m^2/gm depending on its components. The damage could occur through breaking apart and then fines migrate to plug the pores.

The interactions between rock and fluid in sedimentary formations can be (1) chemical reactions of sensitive-rock-minerals with incompatible fluids and/or (2) physical processes as a result of high flow rates and pressure gradients. The solubility tests showed that clay minerals have major impact on the ion type and concentration of precipitates in sandstone cores (Yang et al., 2012).

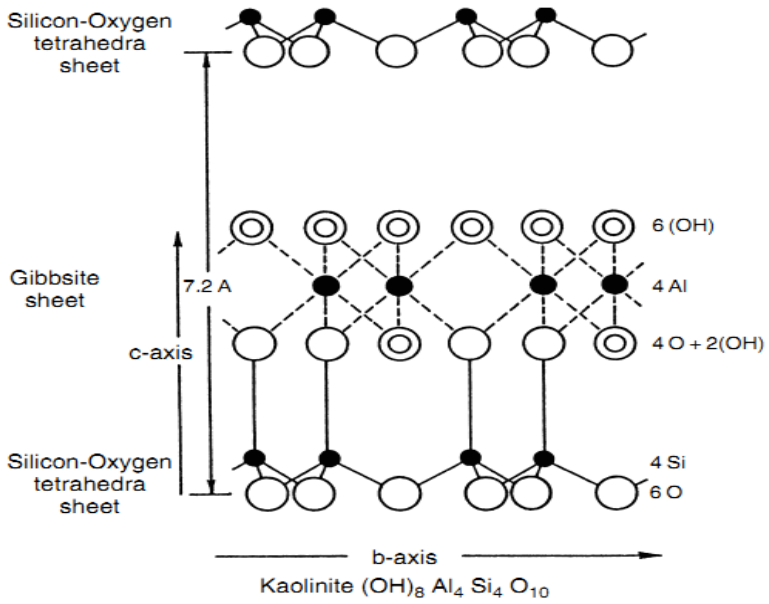


Figure 2 Schematic Description of The Crystal Structure of Kaolinite (Civan 2007).

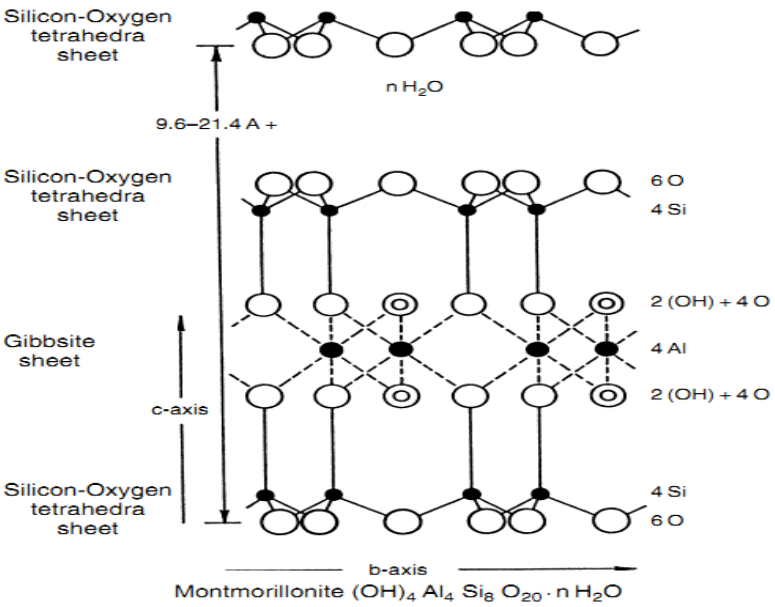


Figure 3 Schematic Description of The Crystal Structure of Montmorillonite (Civan 2007).

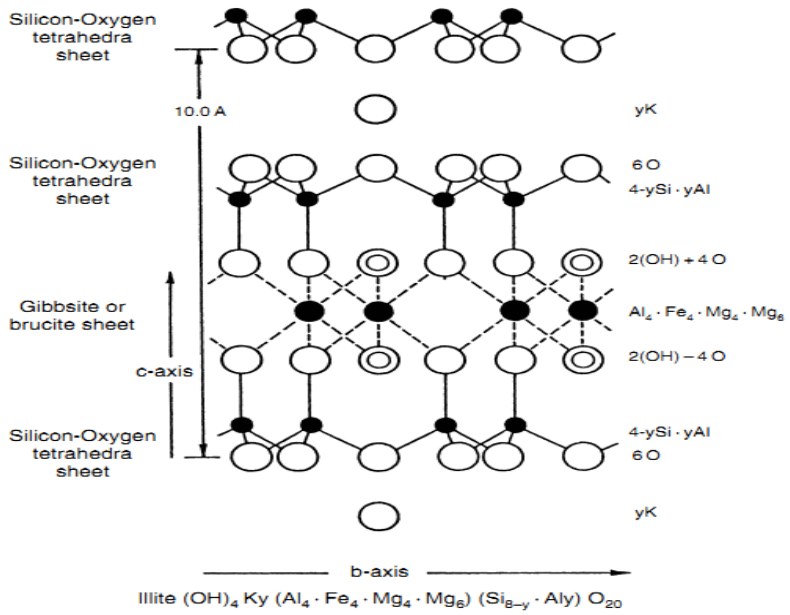


Figure 4 Schematic Description of The Crystal Structure of llite (Civan 2007).

CHAPTER 2

LITERATURE REVIEW

2.1 Mud Acid

Hydrochloric acid (HCl), hydrofluoric acid (HF) or HCl/HF mixture are the most commonly used acids to dissolve minerals in sandstone formations. Interaction of these acids with minerals such as clays and feldspars may cause damage in sandstone formations. Mud acid generally refers to 3 wt. % HF / 12 wt. % HCl. A typical sandstone acidizing job consists of injecting HCl acid as pre-flush then followed by mud acid. An aqueous solution of non-damaging salt such as ammonium chloride or clean solvent such as diesel oil is used to displace the HCl/HF from the tube or the wellbore during the after flush stage. In mud acid, the role of hydrochloric acid (HCl) is to keep the reaction products soluble while hydrofluoric acid (HF) is used to dissolve aluminosilicates.

For many years, the standard treatment consisted of 12 wt. % HCl and 3 wt. % HF mixture preceded by a 15 wt. % HCl pre-flush for sandstones. McLeod (1984) suggested guidelines for acid selection (**Table 2**) which can be taken as starting points in treatment design. Later in 2000, McLeod and Norman modified the selection criteria (**Table 3**).

Injecting HCl in cores containing illite and chlorite (high surface area) will cause reaction between the acid and these clays. Consequently, some reaction products precipitate causing increase in the pressure drop and the viscosity of the acid. Moreover, migration

of these precipitates may plug the pores. In 1990, Simon et al. reported that chlorite is more attackable than illite and kaolinite by HCl acid. HCl attacks chlorite and illite to produce an amorphous silica residue (Simon et al., 1990). As a result of that, it will weak the clay structure and makes it more sensitive to fluid flow. Thomas et al., (2001) illustrated that HCl degraded illite and chlorite in the tested cores from actual producing sandstone reservoirs which led to potential core damage.

HF acid can dissolve feldspar, carbonates, clays, micas and quartz. The primary purpose of using HF is to remove clays. The solubility of various clay minerals (kaolinite, chlorite and illite) in HF acid is function of concentration, reaction time and temperature. The secondary reaction between clays and HF occurred at high temperatures and the ratio of Si/Al decreased. HF acid reacts with clays at weight ratio of 10:1 (Zhou et al., 2013). Carbonates in sandstone should be removed with a pre-flush of HCl to avoid CaF_2 precipitation. **Table 4** shows the solubility of different minerals in HCL and HCL/HF mixture acids (Simon et al., 1990). **Table 5** shows the reaction of mud acid with different minerals.

Table 2 Sandstone Acidizing Fluid Selection Guidelines (McLeod 1984).

Pre-flush fluids			
Mineralogy	Permeability		
	>100 mD	20-100 mD	<20 mD
<10% silt and <10% clay	15% HCl	10% HCl	7.5% HCl
>10% silt and >10% clay	10% HCl	7.5% HCl	5% HCl
>10% silt and <10% clay	10% HCl	7.5% HCl	5% HCl
<10% silt and >10% clay	10% HCl	7.5% HCl	5% HCl
Main Acid Fluids			
	>100 mD	20-100 mD	<20 mD
<10% silt and <10% clay	12% HCl -3%HF	8% HCl -2%HF	6% HCl -1.5%HF
>10% silt and >10% clay	13.5% HCl - 1.5%HF	9% HCl -1%HF	4.5% HCl - 0.5%HF
>10% silt and <10% clay	12% HCl -2%HF	9% HCl -1.5%HF	6% HCl -1%HF
<10% silt and >10% clay	12% HCl -2%HF	9% HCl -1.5%HF	6% HCl -1%HF

Table 3 Recommended Acid Type and Strength For Sandstone Acidizing (McLeod and Norman (2000)).

HCl solubility > 20%	Use HCl only
High-perm sand (k > 100 mD)	
High quartz (80%), low clay (<5%)	10% HCl – 3 % HF[a]
High feldspar (>20%)	13.5 % HCl - 1.5 % HF[a]
High clay (>10%)	6.5 % HCl – 1% HF[b]
High iron chlorite clay	3 % HCl – 0.5 % HF[b]
Low perm sand (k<10mD)	
Low clay (< 5 %)	6% HCl – 1.5 % HF[c]
High chlorite	3% HCl – 0.5 % HF[d]
[a] pre-flush with 15 % HCl [b] pre-flush with sequestered 5 % HCl [c] pre-flush with 7.5 % HCl or 10 % acetic acid. [d] pre-flush with 5 % acetic acid.	

Table 4 Solubility of Different Minerals in Mud Acid and HCl (Simon et al., 1990).

Minerals	Solubility	
	HCl	HCl/HF
Quartz	No solubility	Very low
Feldspars	No solubility	Low to moderate
Kaolinite	No solubility	High
Illite	No solubility	High
Smectite	No solubility	High
Chlorite	Low to moderate	High
Calcite	High	High, CaF_2 is ppt.
Dolomite	High	High, CaF_2 is ppt.

Table 5 Primary Chemical Reactions of Mud Acid With Different Minerals (Geo et al., 2011).

Mineral / Acid	Reaction
Montmorillonite (bentonite)-HF/HCl	$Al_4Si8O_{20}(OH)_4 + 40HF + 4H^+ \leftrightarrow 4AlF_2^+ + 8SiF_4 + 24H_2O$
Kaolinite HF/HCl	$Al_4Si_8O_{10}(OH)8 + 40HF + 4H^+ \leftrightarrow 4AlF_2^+ + 8SiF_4 + 18H_2O$
Albite(sodium feldspar)-HF/HCl	$NaAl_3Si_8O_8 + 14HF + 2H^+ \leftrightarrow Na^+ + AlF_2^+ + 3SiF_4 + 8H_2O$
Orthoclase-HF/HCl	$KAl_3Si_8O_8 + 14HF + 2H^+ \leftrightarrow K^+ + AlF_2^+ + 3SiF_4 + 8H_2O$
Quartz- HF/HCl	$SiO_2 + 4HF \leftrightarrow SiF_4 + 2H_2O$ $SiF_4 + 2HF \leftrightarrow H_2SiF_6$

2.1.1 Problems Associated With Mud Acid

There are some problems associated with sandstone acidizing using mud acid. Among these problems: decomposition of clays (illite) in HCl acid which causes formation damage, rapid corrosion rate at high temperatures, precipitation of reaction products such as silica acid ($Si(OH)_4$) (Labrid 1975), precipitation of aluminum fluorides (AlFx,s) in the presence of carbonate, colloidal silica-gel precipitation, silica-gel filming and hydrated silica. Moreover, at high temperatures (above 300°F) -in sandstone reservoirs- the

reaction of HCl is very quick and the clays become unstable (Ali et al., 2002). Using low concentration of HCl and HF will cause precipitation of $Al(OH)_3$ (Al-Shaalan et al., 2000). The reaction of fluosilic acid with cations present in the formation brine produce precipitants $CaSiF_6$, Na_2SiF_6 and K_2SiF_6 (Al-Shaalan et al., 2000):

$$SiF_6^{-2} + Ca^{+2} \rightarrow CaSiF_6 \quad (2.1)$$

$$SiF_6^{-2} + 2Na^{+} \rightarrow Na_2SiF_6 \quad (2.2)$$

$$SiF_6^{-2} + 2K^{+} \rightarrow K_2SiF_6 \quad (2.3)$$

Researchers were investigated many alternatives to overcome the problems that happen during acidizing using mud acid.

2.2 HF Acid

Hydrofluoric acid (HF) has specific reaction properties with silica which make it more effective than HCl for acidizing sandstone formations. The primary chemical reaction between hydrofluoric acid and aluminosilicates in Berea sandstone samples can be expressed as in the following equations (Gdanski 1997):

$$(5 + x)HF + M - Al - Si + (3 - x + 1)H^{+} \rightarrow HSiF_5 + AlF_x^{(3-x)+} + M^{+} + H_2O \quad (2.4)$$

Where: x is the average F/Al ratio and M^{+} stands for cations such as K^{+} and Na^{-}

The secondary reaction of $HSiF_5$ with aluminosilicate can be written as:

$$\frac{x}{5}HSiF_5 + M - Al - Si + (3 - x + 1)H^{+} + H_2O \rightarrow AlF_x^{(3-x)+} + M^{+} + \text{silica gel} \quad (2.5)$$

The tertiary reaction will exist when aluminum fluoride complexes react with clay which produce more precipitation of silica gel:

$$yAlF_x^{(3-x)+} + (x-y) - Al - Si + 3(x+y)H^+ \rightarrow xAlF_y^{(3-y)+} + (x-y)\text{silica gel} \quad (2.6)$$

Where y is the fluoride number coordinated with aluminum after tertiary reaction, y < x.

Reaction of hydrofluoride with $CaCO_3$ will form (CaF_2) when (Al-Shaalan et al., 2000).

$$CaCO_3 + 2HF \rightarrow CaF_2 + H_2O + CO_2 \uparrow \quad (2.7)$$

Smith et al., (1986) used buffered HF acid system (12% H_3PO_4/3% HF) to acidize Berea Sandstone core sample containing 9% carbonate. The buffered HF acid system was able to prevent secondary precipitation of silicon or aluminum complexes because the phosphoric acid kept the pH low. Moreover, the unique surface reactions between calcite and (12% H_3PO_4/3% HF) prevent large amount of calcium cations from being brought into solution from reaction with the carbonate content in the sandstone. Low corrosion rates were reported using buffered regulated organic acid and buffed regulated HF acid systems for temperature up to 550^{o}F and pH range from 4.5 to 5.9 (Scheuerman 1988). However, the main problem of HF-based acid is the sand production (Nasr-El-Din et al., 2014).

2.3 Retarded Acids

Generally, retarded acids are used when the damage in the sandstone formation is deep. Kunze et al., (1983) suggested Fluoboric acid (HBF_4) instead of conventional mud acid to overcome the problem of rapid reaction with clays at formation temperature. However,

Fluoboric acid system has the silica potential precipitation problem associated with HF acidizing.

Al-Anazi et al., (2000) used retarded HF (RHF) to stimulate water injector wells in sandstone formation. Core samples showed high iron content thus using iron-control agent was suggested. Adding 15 wt. % pre-flush of NH_4Cl enhanced the permeability because it was able to move potassium and sodium from the sample and reduce precipitation of fluosilicates. Using 15 wt. % HCl acid enriched the RHF acid and improved the permeability. Nevertheless, retarded acids still have the same problems of mud acid.

Jaramillo et al., (2010) documented that Fluoboric acid has the ability to control fine migration and stabilize the clay. An organic- Fluoboric acid system was successfully formulated to acidize low temperature (< 140^oF) high clay content (kaolinite > 30 % with feldspar) sandstone reservoir. The concentration of free HF in the acid was optimized with clay mineralogy and clay surface area because low concentration may cause fine migration and plug the pores whereas high concentration will lead to deconsolidation and precipitation of clay.

Ji et al., (2014) investigated the reaction of fines control acids consist of 15 wt. % HCl, 1.5 wt. % HF and 5 wt. % $AlCl_3.6H_2O$ in sandstone formations contain clays. NMR analysis showed that $AlCl_3$ can retard the reaction of HF with different clays such as illite, kaolinite and bentonite at 75^oF. However, precipitations of H_2SiF_6 and H_2SiF_5 were observed in the spent acid.

2.4 Organic Acids

Many investigators suggested organic acids to acidize sandstone formations to replace conventional mud acid specially in the presence of HCl-sensitive clays due to their retarded nature and low corrosion rates.

In 2013, Shafiq et al. studied different acid combinations: HF/HCl, HF/HCOOH, HF/H_3PO_4, HBF_4/HCl and HBF_4/HCOOH. Hydrofluoric acid and Fluoboric acid were used to dissolve feldspar and clays. In addition to that, hydrochloric acid, phosphoric acid and formic acid were added to control the speed of the reaction, to maximize the penetration depth and maintain the pH of the solution. Analysis of the porosity, permeability, color change, strength and mineralogy showed that most of these combinations gave better results than mud acid. The most successful blend was (3% HF: 9% H_3PO_4 and 3% HBF_4:12%HCOOH).

Al-Harbi et al., (2013) did core flood tests to investigate the ability of organic acids when they combined with HF to eliminate the carbonaceous and siliceous minerals from Berea sandstone at 250^oF. Citric-HF acid was able to dissolve significant amount of calcium and aluminum and an increase in permeability was observed using low HF concentration.

In 2012, Yang et al. used 9 wt. % Formic acid to stimulate sandstone cores. Core flooding tests showed that formic acid/HF reduced the permeability at room temperature. Increasing HF concentration removes more aluminosilicates but causes precipitation of calcium fluoride. 13 wt. % Acetic acid gave the same results of Formic acid with releasing different ions.

In 2011, Al-Harbi et al. tested different organic HF based fluids using formic, acetic and citric acids. Generally, organic-HF acids retarded the interaction with sand and clays compared with mud acid. The reaction rate depends on ratio of organic acid to HF, type of the organic acid and the temperature (the reaction rate increased when the temperature is above 122^{o}F). It was recommended to use organic-HF to stimulate clean sandstones or that contain illite clays. However, severe damage due to precipitation of AlF_3 was reported in the presence of chlorite clays.

Zhou et al., (2013) advised not to use HF-based acid in existence of high amount of kaolinite in sandstone formation and reduce the soaking time to avoid precipitations at high temperature (above 150^{o}C).

Al-Harbi et al., (2012) reported precipitation of AlF_3 after using different organic-HF acids. The amount of precipitates depended on the Al/F ratio. At pH 4.3 iron cations deposited in the form of Na_3FeF_6 which re-dissolved in citric-HF at higher pH values. It could be noticed that fluoride concentration, pH value and organic-HF type were the factors that controlled the amount and type of precipitates.

2.5 Chelating Agents In Sandstone Acidizing

Hydrofluoric based acids were widely used to stimulate sandstone formations. However, many problems were reported such as rapid spending rate, subsequent precipitation and decomposition of sensitive clays. Researchers proposed new acid systems based on chelating agents as another approach. Chelating agents are generally weaker than HCl and organic acids, so their reaction rate is slow.

2.5.1 Chelation Chemistry

Chelating agents are complex chemical compounds which enhance the affinity by the ability of their molecules to form several bonds (multi-dentate ligand) to a metal ion. Chelation is the process of binding the chelating agent to any compound by forming a ring shape around it. The chelated metal will be more stable than non-chelated metal which has the same general chemical formula. **Figure 5** shows the chemical structure of HEDTA, EDTA and DTPA chelating agents. Aminopolycarboxylic acids loss protons to reach the ionized state as follows:

$$H_4Y \rightleftharpoons H_3Y^{-1} + H^+ \quad (2.8)$$

$$H_3Y^{-1} \rightleftharpoons H_2Y^{-2} + H^+ \quad (2.9)$$

$$H_2Y^{-2} \rightleftharpoons HY^{-3} + H^+ \quad (2.10)$$

$$HY^{-3} \rightleftharpoons Y^{-4} + H^+ \quad (2.11)$$

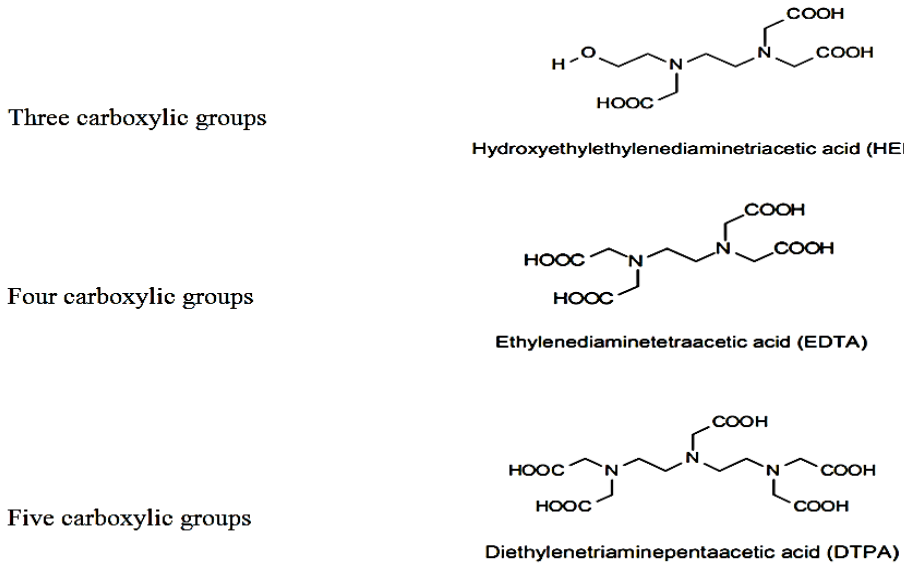


Figure 5 Chemical Structure of HEDTA, EDTA and DTPA Chelating Agents (Mahmoud et al., 2011a).

The distribution of ionic species depends on the pH of the solution and the equilibrium constant required for each reaction. The general formula of the aminopolycarboxylic acids chelating agents with metal ions gives 1:1 complexes in ordinary conditions with most metal ions and can be expressed as:

$$M^{+n} + Y^{-4} \rightleftharpoons MY^{(n-4)} \quad (2.12)$$

The stability of the chelating agents K_{MY} can be defined as the ratio of the chelated cations in equilibrium with the free cations and chelating agents in solution. **Table 6** shows the stability constants of HEDTA, EDTA and DTPA.

$$K_{MY} = \frac{[MY^{(n-4)}]}{[M^{+n}][Y^{-4}]} \quad (2.13)$$

Table 6 Stability Constant For Different Cations With Different Chelating Agents (Frenier et al. 2001 and Mahmoud et al.,2011)

Chelating agent	Stability constant (Log KMY)			
	Fe^{3+}	Ca^{2+}	Mg^{2+}	Al^{3+}
HEDTA	19.8	8.4	7	14.4
EDTA	25	10.7	8.83	16.5
DTPA	28	10. 9	9.3	18.7

Many chemical reactions happen at the rock-acid interface. There are mainly three reactions can control the dissolution process: water attack, proton attack or ligand attack. Fredd and Fogler (1997) reported that for high pH water/ligand attack controls the

reaction. On the other hand, at low pH the reaction is controlled by proton attack. Calcium and carbonate products will be captured and adsorbed on the surface as following during dissociation process:

$$L^{4-} \leftrightarrow L^{4-}_{(ads)} \tag{2.14}$$

$$L^{4-}_{(ads)} + CaCO_3 \leftrightarrow CaL^{2-}_{(ads)} + {CO_3^{2-}}_{(ads)} \tag{2.15}$$

$$CaL^{2-}_{(ads)} \leftrightarrow CaL^{2-}_{(i)} \tag{2.16}$$

$${CO_3^{2-}}_{(ads)} \leftrightarrow {CO_3^{2-}}_{(i)} \tag{2.17}$$

Where ads and I indicate species adsorbed at the surface and located at the solid-liquid interface, respectively.

Frenier et al. (2001) suggested that at high pH HEDTA reacts with calcite as in the next equation:

$$CaCO_3 + Na_3HEDTA \leftrightarrow NaCaHEDTA + Na_2CO_3 \tag{2.18}$$

At moderate pH the reaction will be controlled by both ligand and proton attacks. This situation makes the determination of the diffusion coefficients very difficult.

2.5.2 Chelating Agents as Stimulation Fluids

Chelating agents were used in oil industry to control undesirable reactions of cations with formation minerals to prevent the precipitation of solids byproduct. Fernier et al., 2000 used EDTA and HEDTA to control the precipitation of ferric and ferrous hydroxide, to remove scale and as stimulation fluid. In 1997, Fredd and Fogler introduced EDTA,

CDTA and DTPA chelating agents as stimulation fluids for carbonate formations as an alternatives for conventional HCl acid. Frenier et al., (2003) presented hydroxyethyliminodiacetate (HEIDA) which found to be more biodegradable, environmentally better than EDTA or DTPA and soluble in acid for wide range of pH.

Ali et al., (2002) stimulated gas wells in sandstone reservoirs damaged with carbonate and contained clays at 300^{o}F. For Berea sandstone core, Na_3HEDTA showed better results compared with HCl. Na_3HEDTA at pH 4 was preferred to mineral or organic acid. Low pH Na_3HEDTA and HEDTA was used to acidize West Africa sandstone cores at high temperatures (300^{o}F). The major advantage of using HEDTA was the reduction in reaction and corrosion rate which led to enhance the permeability and meanwhile maintain the well equipment.

Parkinson et al., (2010) reported that HEDTA was effective to acidize Pinda West Africa sandstone containing carbonate (2% - 100%) at temperature up to 300^{o}F. HEDTA showed low corrosion of tubular.

In 2011, Mahmoud et al. used GLDA (glutami-N, N-diacetic acid) chelating agent with concentration 0.6 M to stimulate Berea sandstone cores which have 8 wt. % clays at temperature up to 300^{o}F with different pH values between 1.7 and 13. GLDA was able to increase the permeability and porosity. Moreover, the lower the injection rate provided the contact time of GLDA with the rock and enabled cations to be dissolved. In addition to that, high thermal stability was observed up to 300^{o}F during core flooding experiments. GLDA showed better permeability results than HEDTA and HCl acids at pH 4 and 300^{o}F.

De Wolf et al., (2014) studied four different Aminopolycarboxilic acid chelating agents i.e. GLDA, ASDA, MGDA and EDG. GLDA was the better solution at low pH among these acids. It had less corrosion of low carbon and Cr-13. GLDA was more effective in enhancing permeability in sandstones and had higher calcite dissolution capacity.

In 2014, Nasr-El-Din et al. presented a successful application of GLDA chelating agent to stimulate oil well drilled in offshore sandstone reservoir. Low corrosion rate was proved based on the analysis of flow back samples (the concentration of iron and manganese were very low) comparing with previous treatment using 15 wt. % HCl or 13.5/1.5 HCl/HF acids. The field treatment was done in stages. Firstly, pre-flush using xylene has been conducted. After that, 25 wt. % of GLDA, a water wetting surfactant and corrosion inhibitor were pumped in the main stage. Then the mixture was displaced to the target formation using diesel. Good enhancement in oil production was obtained after allowing the fluids to soak for 6 hours without any fine migration or sand control problems.

Sokhanvarian et al., (2012) analyzed the thermal stability of solution (0.4 M to 0.6 M) of different chelating agents including HEDTA, GLDA, NTA, EDTA and their salts. Core flood tests were conducted on Berea sandstone cores. Decomposition of most of these chelating agents were observed at 350^{o}F which damaged the cores. Only thermal decomposition product of GLDA did not cause any damage. By-products of thermal decomposition were iminodiacitic (IDA), oxotetrahydrofuran-2 carboxylic acid (HEIDA), hydroxyglutaric acid and acetic acid.

Mahmoud et al. (2015) used GLDA chelating agent to stimulate Berea sandstone cores which have 8 wt. % clays at temperature up to 300°F with different pH values between 1.7 and 13. GLDA showed better permeability results than HEDTA and HCl acids at 300°F. They used GLDA combined with HF and the maximum increase in core permeability was achieved with the optimum ratio of GLDA/HF concentration of 20 wt. % GLDA/1 wt. % HF. Al-Dahlan et al. 2013, studied the interaction between Ca^{2+} and Al^{3+} with EDTA-HF fluid. They concluded that the precipitation of AlF_3 will happen when the ratio of aluminum to flour exceeds a critical ratio.

2.6 Seawater Based Acids

Offshore stimulation jobs are costly operations due to the cost of transporting fresh water to the offshore platforms. Seawater was introduced to be used either to prepare or flush the acids to minimize the cost of logistic supply of the fresh water. However, seawater has the problem of scale precipitation. Sulfate ions from seawater combine with calcium, barium, or strontium ions in the formation brine or with calcium in the spent acid to produce sulfate scale. He et al., (2011) prepared HCl using seawater and he found that calcium sulfate precipitated at different stages of the acidizing process due to the use of seawater. Oddo et al. (1991) reported the same phenomena when seawater and KCl were used to post flush the mud acid from offshore wells after treatment.

Mahmoud (2014) used EDTA, HEDTA, and HEIDA (at pH of 11) to prevent and remove the damage caused by $CaSo_4$ during using high and low salinity seawater in Berea sandstone cores. CT-number was used to evaluate the damage caused by calcium sulfate across the cores.

CHAPTER 3

RESEARCH OBJECTIVES AND METHODOLOGY.

3.1 Research Motivation

Many acids such as conventional mud acid, HF and organic acids were suggested to reduce the skin in sandstone formations and enhance the permeability. However, problems could be encountered during sandstone acidizing using these acids. Among those problems, decomposition or swelling of clays when incompatible fluid is used, rapid corrosion rate at high temperatures and precipitation of reaction products.

Researchers used chelating agents widely in oil industry as iron capturing additives, to remove scale and recently as a stand-alone stimulation fluid for sandstone reservoirs. The efficiency of many types of chelating agents were tested for sandstone reservoirs such as GLDA, EDTA and HEDTA and their salts. In this work, a new acid will be formulated as a combination of chelating agent and potassium carbonate catalyst. Moreover, the efficiency of using seawater based fluids will be examined also as cost effective approach.

3.2 Research Objectives

The objectives of this research are:

1. Introduce new formulation using DTPA chelating agent and potassium carbonate catalyst for sandstone acidizing

2. Identify the optimum conditions of the formulated fluid in terms of DTPA concentration and catalyst/DTPA ratio using seawater and deionized water at high pH
3. Determine the effectiveness of the catalytic-DTPA acid as a stand-alone stimulation fluid for both Berea and Bandera sandstone and compares this to EDTA and HEDTA chelating agents
4. Examine the rock integrity after stimulating Berea and Bandera cores with EDTA and DTPA at high pH by acoustic measurements

3.3 Research Methodology and Experimental Work

3.3.1 Materials

EDTA, HEDTA and DTPA chelating agents (obtained from local supplier) with initial concentration of 40 wt. % were used in this study. They were diluted using deionized water and seawater. Synthetic seawater was prepared using salts (**Table 7**). Potassium carbonate catalyst was added to the chelating agents with different concentrations. 3 wt. % KCl was the brine used to saturate the cores and pre-flush and post flush during core flooding runs. Standard Berea and Bandera Gray sandstone were used during the experiments.

Table 7 Arabian Gulf Seawater Salts.

Salt	Concentration (gm/L)
$NaHCo_3$	0.2382
Na_2SO_4	6.5754
$CaCl_2.H_2O$	2.3945
$MgCl_2.6\ H_2O$	18.0539
NaCl	40.2738

3.3.2 Formulation of the New Fluids

New fluids were formulated using potassium carbonate catalyst and chelating agents with different concentrations. A solubility tests were conducted to determine the optimum catalyst / chelating agent's ratio and its concentration.

A pH meter instrument (**Figure 6**) was used to measure the pH of the solutions to check their stability with deionized water and seawater. Different chelate solutions with different concentrations diluted using deionized water and seawater were prepared. Viscosity of the solutions was measured with different temperatures using capillary tube viscometer (**Figure 7**) for the pH and concentration defined before.

Table 8 shows the viscosity of different solutions which were used during core flooding experiments. **Figure 8** shows the viscosity of 3 wt. % KCl at different temperaures.

Figure 6 pH Meter.

Figure 7 Capillary Tube Viscometer.

Table 8 Viscosity of Different Solutions of EDTA and DTPA at pH of 11.

Fluid	Density, gm/cm^3	viscosity, cP
E20-DI	1.127	2.34
E20C3-DI	1.136	2.55
E20-sea	1.121	2.12
E20C3-sea	1.134	2.23
D20-DI	1.141	2.39
D20C3-DI	1.155	2.58
D20-sea	1.156	2.32
D20C3-sea	1.171	2.37

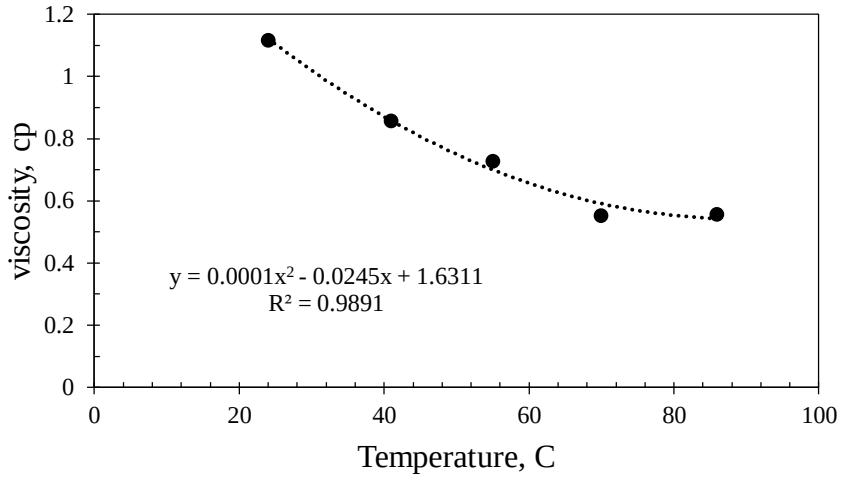


Figure 8 Viscosity of 3 wt. % KCl at Different Temperatures.

3.3.3 Solubility Tests

A solubility tests of Bandera and Berea sandstone in chelating agents were conducted to identify the optimum concentration of the acid. The effect of adding the catalyst, using seawater or deionized water and temperature was considered during the tests. The solubility experiments were conducted as following:

1- At first a crushed powder of the Berea and Bandera samples was prepared
2- Solubility tests based on 1:1 molar ratio were performed using chelating agents with different concentrations range from 5 to 25 wt. % to determine the optimum acid concentration.
3- The potassium carbonate catalyst was added to the optimum acid concentration by 1, 3, 6 and 9 wt. % to specify the optimum catalyst ratio.
4- The chelating agents were diluted using deionized water and seawater.
5- The solubility tests were done at room temperature and at 150^{o}F.

3.3.4 Core Samples Saturation

Berea and Bandera core samples were prepared to the acidizing treatment. 1.5 inches diameter and 2 - 6 inches length Bandera and Berea sandstone samples are used for the core flooding runs. The procedures for core sample preparation were as following:

1- Dry the core sample firstly to remove any water humidity for 24 hours.
2- Measure the dry weight.
3- The core samples were saturated under vacuum for 3 hours. Then they were saturated by 3 wt. % potassium chloride (KCl) under 2500 psi pressure using a pump for one day.

4- Check the pressure after one day to make sure that the cores are well saturated with the brine.

5- Measure the wet weight after saturation.

6- Calculate the pore volume and porosity of the cores using weight difference method.

3.3.5 Core Flood Experiments

A core flooding system with heating capacity up 300^{o}F was used to inject the acids. **Figure 9** shows the schematic of the core flooding system. The stimulation steps are as follows:

1- Fill the accumulators with KCl brine and chelating agent solution.

2- Insert the core sample into the core holder and tighten the inlet and outlet of the core holder against the core sample.

3- Connect the core holder lines to the core flooding system lines.

4- Set the temperature to the required value and allow enough time for the core sample to be heated (about 6 hours).

5- Apply the required net overburden on the core sample to insure no leak in the core holder. Increase the overburden and back pressure gradually to avoid damaging the sleeve. The overburden set to be 2000 psi and the back pressure was 1000 psi for all the experiments.

6- Inject KCl brine at specified injection rate into the core sample until flow stabilization. At this step, core permeability was estimated.

7- After pre-flushing, the chelating solution was injected at different rates. The pressure drop was monitored with time until the required pore volumes were injected. Effluents from some intervals were collected for analysis.

8- After injecting the chelating agent solution, KCl was injected again to post flush the core sample and to determine the core permeability after stimulation.

Figure 9 Core Flooding System.

3.3.6 Effluents Analysis

During the acidizing treatment experiments, samples at each specified pore volume will be collected. Inductively coupled plasma (ICP) device (**Figure 10)** was used to analyze the effluents in order to determine the type and concentration of chelated cations and understand the working mechanism of potassium carbonate catalyst.

Figure 10 Inductively Coupled Plasma (ICP) Device.

3.3.7 Computed Tomography Scanning

To evaluate the effectiveness of the matrix stimulation with DTPA, cores were scanned before and after acidizing. The main objective of core scanning is to detect the alterations of properties of the rock that may happen inside the cores. Computed Tomography (CT) scan was used to evaluate the core samples. **Figure 11** shows the CT scan instrument.

Figure 11 CT Scan Instrument.

3.3.8 Acoustic System

The elastic moduli were used to evaluate the rock integrity after using the new formulation. Velocity of s-waves and p-waves were measured using acoustic system before and after stimulation. **Figure 12** shows the acoustic system.

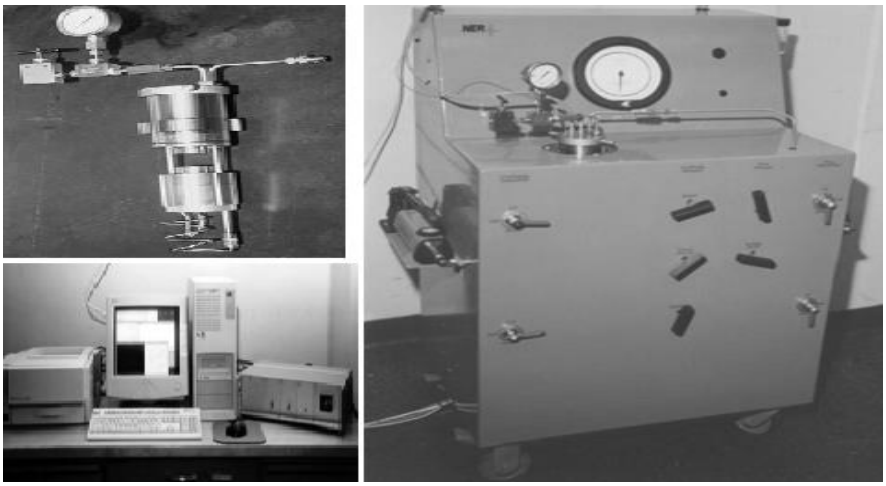


Figure 12 Acoustic System.

CHAPTER 4

DEVELOPMENT OF NEW FORMULATION FOR SANDSTONE ACIDIZING

4.1. Introduction

Seawater is playing a major role in current practice in the offshore stimulation to cut off the cost associated with logistic supply of deionized water. Recently, chelating agents were introduced as standalone stimulation fluids for sandstone formations. The objective of this part is to introduce new formulation for sandstone acidizing that consists of chelating agents diluted with seawater and deionized water combined with potassium carbonate catalyst for sandstone formations. This is the first time to introduce DTPA (diethylene tri-amine penta-acetic acid) and potassium carbonate as a catalyst in sandstone acidizing.

Solubility experiments were conducted to determine the optimum concentration of the chelating agent and potassium carbonate catalyst. Solutions of EDTA (Ethylene diamine tetra-acetic acid), HEDTA (hydroxyl ethylene diamine tri-acetic acid) and DTPA (diethylene tri-amine penta-acetic acid) chelating agents at high pH combined with potassium carbonate were used. Moreover, the effect of temperature on the solubility was

examined. Core flooding experiments were conducted to evaluate the efficiency of the new formulated fluids as a standalone stimulation fluid for sandstone formations.

4.2 Methodology

4.2.1 Materials

EDTA, HEDTA, and DTPA chelating agents (at pH of 11) with initial concentration of 40 wt. % were used to conduct solubility tests on crushed Berea and Bandera sandstone samples. Potassium carbonate was added to the chelates as a catalyst. Seawater was prepared by adding salts to the deionized water; the composition of the seawater is listed in Table 9. The chelating agents were prepared using deionized water and seawater.

Berea and Bandera core samples with 2 inches length and 1.5 inches diameter were used in the core flooding experiments. 3 wt. % KCl was used as brine to saturate, pre-flush, and post-flush the cores. DTPA 20 wt. % and 20 wt. % DTPA/3 wt. % K_2CO_3 were used in the flooding experiments for Bandera sandstone cores.

4.2.2 Solubility Tests

The solubility tests were conducted using 1:1 molar ratio to achieve maximum solubility. **Table 10** illustrates the molecular weight of chelating agents (HEDTA, EDTA, and DTPA). **Table 11** shows the mineral composition of Berea and Bandera sandstone. Fluids with concentrations range from 5 wt. % to 25 wt. % were used to determine the optimum chelate concentration at pH = 11.

Table 9 Composition of Seawater (Mahmoud 2014)

Ions	Concentration (ppm)
Sodium	18,300
Calcium	650
Magnesium	2,110
Sulfate	4,290
Chloride	32,200
Bicarbonate	120
Total Dissolved Solids	57,670

Table 10 Molecular Weights of Chelating Agents.

Acid	formula	Molecular weight (gm/mole)
Na_3EDTA	$C_{10}H_{13}N_3O_8 \bullet Na_3$	372.19
Na_3HEDTA	$C_{10}H_{15}N_3O_7 \bullet Na_3$	358.21
Na_3DTPA	$C_{14}H_{23}N_3O_{10} \bullet Na_3$	462.32

Table 11 Mineral Composition of Bandera and Berea Sandstone Samples (Civan 2007, Economides et al., 2012 and Mahmoud et al., 2015).

Mineral	Concentration of Mineral, wt. %		Molecular weight (mass/mole)
	Berea	Bandera	
Quartz	86	57	60.1
Dolomite	1	16	184.4
Calcite	2	--	100.1
Feldspar	3	--	159.3
Kaolinite	5	3	516.4
Illite	1	10	389.34
Chlorite	2	1	67.4518
Plagioclase	--	12	278.3
M.W.	91.37	152.26	

4.2.3 Experiments Set Up

The specified weight of Berea and Bandera samples was measured using a balance as well as the filtration paper. The fluids were prepared and well mixed by magnetic stirrer. The pH meter was used to check the pH instantaneously during the preparation. All the samples were left for 24 hours to react. After that, filtration paper on a conical flask connected to vacuum pump was used to filter the prepared samples. The solids and fluids were collected after filtration. Then the filtration papers containing the solid particles were dried in the oven for 6 hours. After that weights were recorded to calculate the solubility ratio.

4.2.3 Core flooding Experimental Procedures

At first the cores were saturated using 3 wt. % KCl before flooding. Then they were loaded to the core holder. The cores and the fluids were heated up to 250^{o}F for at least 6 hour. 2000 psi overburden pressure was applied to the core samples and the back pressure was 1000 psi during the experiments. 3 wt. % KCl brine was used for pre-flush and post flush stages. Three injection rates were used for the flush stages 4, 2 and 1 cm^3/min. The fluid volume used during the flooding experiment was 6 pore volumes.

4.3 Results and Discussion

4.3.1 Solubility Tests at Room Temperature

Firstly, the solubility tests were carried out at room temperature using EDTA, HEDTA and DTPA. The optimum concentration of the chelating agents found to be at 20 wt. % at room temperature (**Figure 13-15**). For Berea samples treated using DTPA, the solubility

ratio was 6.2 % and 5.3 % using deionized water and seawater respectively. For Bandera the ratio increased to 13 % after using deionized water and 12.5 % for solution diluted with seawater (**Figure 16**).

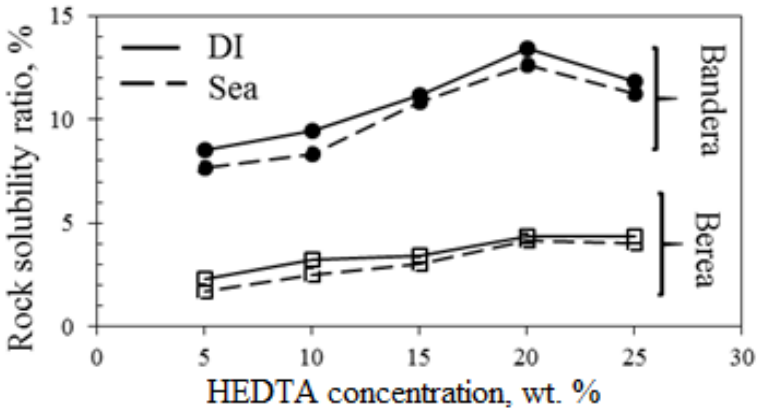


Figure 13 Solubility of Berea and Bandera in HEDTA Solutions at pH of 11 with Different Concentrations Diluted Using Deionized Water and Seawater at Room Temperature.

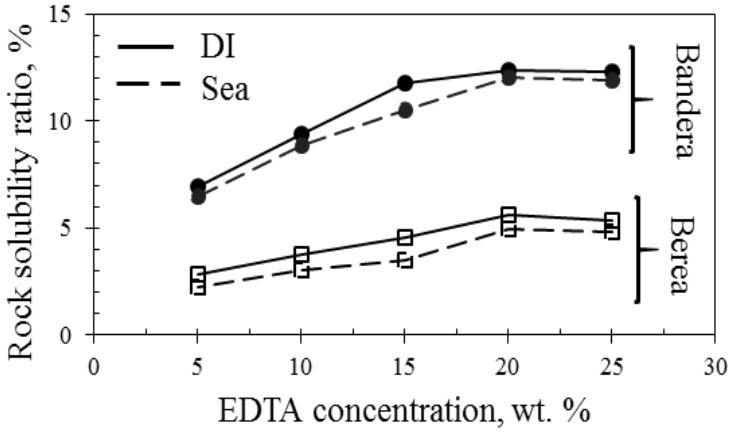


Figure 14 Solubility of Berea and Bandera in EDTA Solutions at pH of 11 with Different Concentrations Diluted Using Deionized Water and Seawater at Room Temperature.

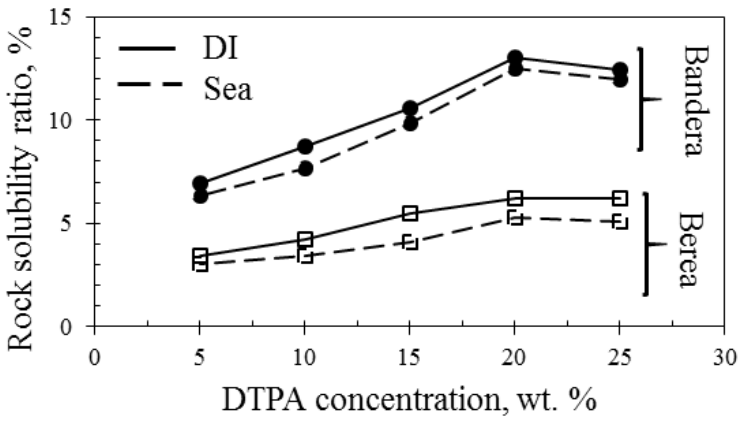


Figure 15 Solubility of Berea and Bandera in DTPA Solutions at pH of 11 with Different Concentrations Diluted Using Deionized Water and Seawater at Room Temperature.

At concentration of 25 wt. % of the chelating agents (which exceeded the optimum) there was reduction in the solubility ratio in some cases of Bandera samples. This reduction is due to the increase in viscosity of the fluids after chelating of dissolvable cations and it will retard the reaction. Mahmoud et al., (2010) pointed out this phenomena for GLDA chelating agent and Mostofizadeh and Economides (1994) reported similar note for HCl

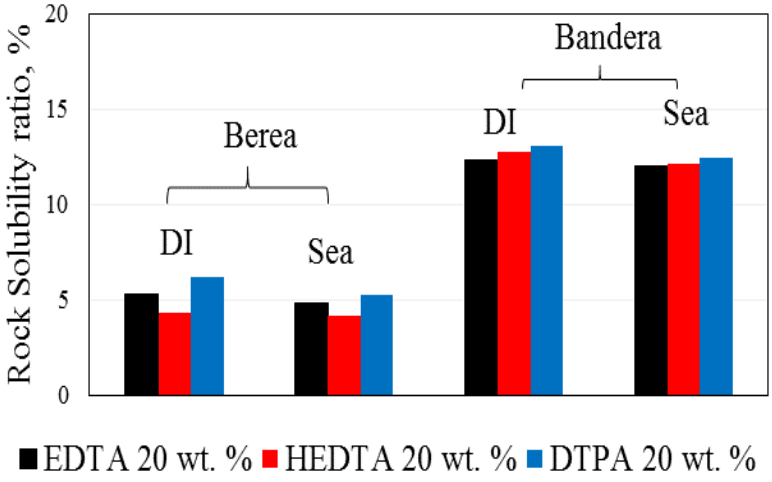


Figure 16 Solubility of Berea and Bandera in 20 wt. % HEDTA, EDTA and DTPA Solutions at pH of 11 Diluted Using Deionized Water and Seawater at Room Temperature.

4.3.2 Effect of adding potassium carbonate at room temperature

The potassium carbonate was added to the chelating agents at different concentrations 1, 3, 6 and 9 wt. %. It was noticed that, adding potassium carbonate up to 3 wt. % enhanced the solubility ratio of both Berea and Bandera sandstone. However, adding more weight of the catalyst did not show more increase. The catalyst enhanced chelation of cations such as Ca^{2+}, Mg^{2+} and Fe^{3+}. As a result of chelating more cations the solubility of the sandstones increased due to dissolving more carbonate and dolomite minerals and capturing ferric from chlorite clay.

Figure 17-19 show the solubility ratio after adding the potassium carbonate to the chelating agents at room temperature. For Berea samples insignificant increase was noticed, approximately 1 % because of low percent of the fast dissolvable minerals (carbonate). The same was noticed for Bandera, the solubility ratio raised to 15.6 % using deionized water.

Chelating agents showed good stability in seawater. The main problem of using seawater based acids is the precipitation of calcium sulfate scale after reaction with carbonates in sandstone formation (Mahmoud 2014). Chelating agents can successfully prevent this problem because they have high affinity to chelate calcium cations.

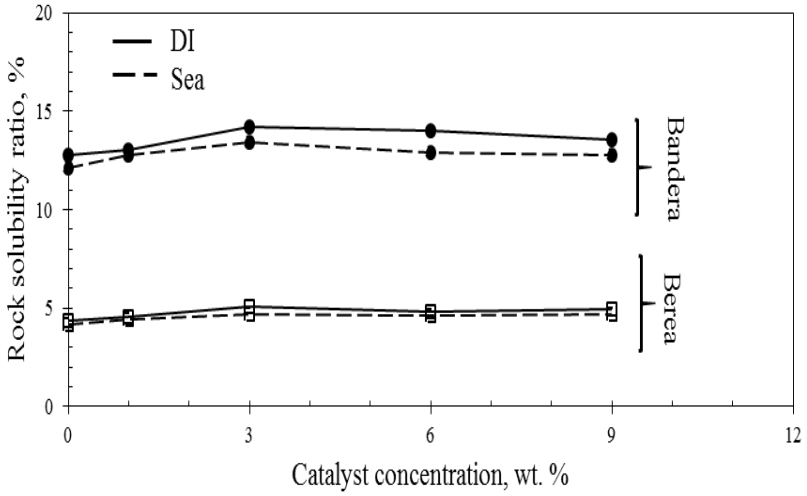


Figure 17 Solubility of Berea and Bandera in 20 wt. % HEDTA Solutions at pH of 11 with Different Concentrations of K_2CO_3 Diluted Using Deionized Water and Seawater at Room Temperature.

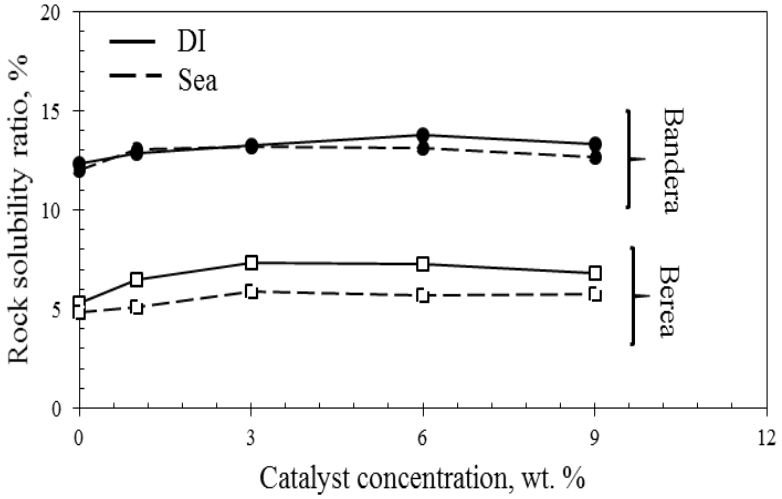


Figure 18 Solubility of Berea and Bandera in 20 wt. % EDTA Solutions at pH of 11 with Different Concentrations of K_2CO_3 Diluted Using Deionized Water and Seawater at Room Temperature.

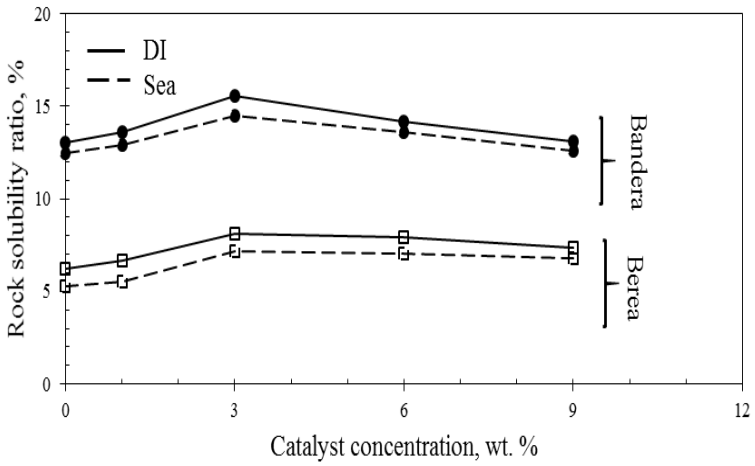


Figure 19 Solubility of Berea and Bandera in 20 wt. % DTPA Solutions at pH of 11 with Different Concentrations of K_2CO_3 Diluted Using Deionized Water and Seawater at Room Temperature.

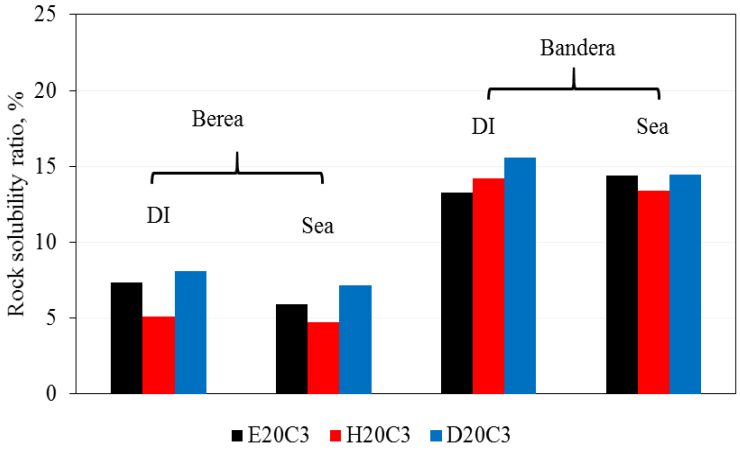


Figure 20 Solubility of Berea and Bandera in 20 wt. % HEDTA, EDTA and DTPA Solutions at pH of 11 After Adding 3 Wt. % Of the Catalyst Diluted Using Deionized Water and Seawater at Room Temperature.

4.3.3 Solubility Tests at 150°F

The same steps were repeated at 150°F (**Figure 21-23** and **Figure 25-27**). It was observed that increasing the temperature enhanced the performance of the chelating agents either before or after adding the catalyst. The most enhancement was recorded for

Bandera samples and it was up to 4 % after adding 3 wt. % of potassium carbonate to 20 wt. % DTPA diluted using deionized water. The red color was clearly seen in the solutions for Bandera samples after heating up which indicates the chelating of Fe^{3+} from chlorite clay. Increasing the temperature will accelerate the chelation process and enable the chelating of additional amount of ferric, calcium and magnesium cations.

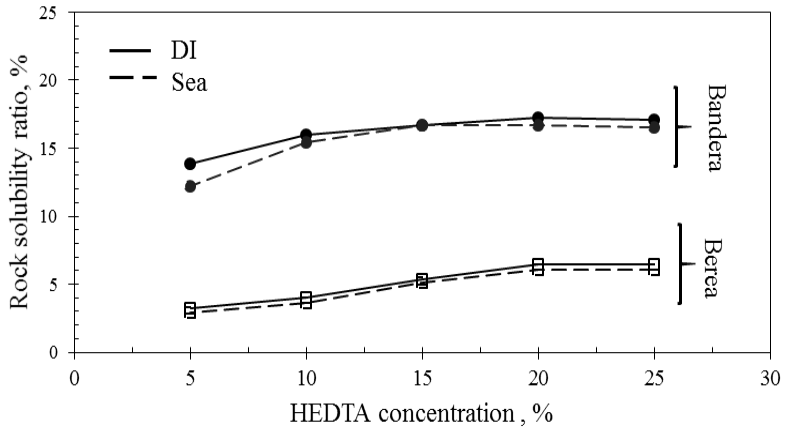


Figure 21 Solubility of Berea and Bandera in HEDTA Solutions at pH of 11 with Different Concentrations Diluted Using Deionized Water and Seawater at 150ºF.

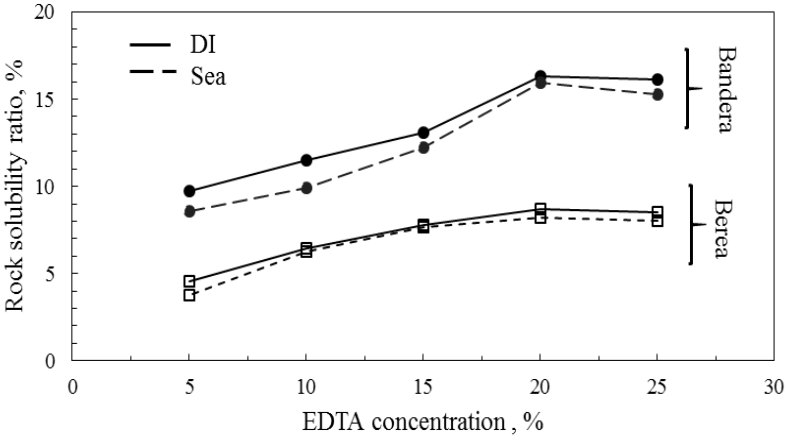


Figure 22 Solubility of Berea and Bandera in EDTA Solutions at pH of 11 with Different Concentrations Diluted Using Deionized Water and Seawater at 150ºF.

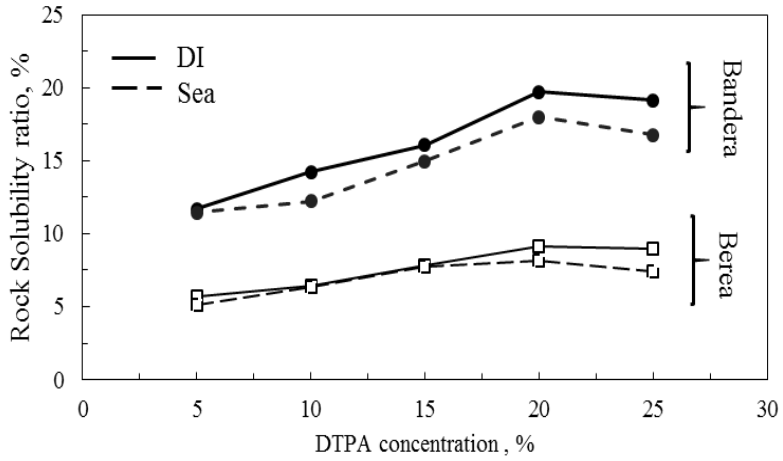


Figure 23 Solubility of Berea and Bandera in DTPA Solutions At pH Of 11 with Different Concentrations Diluted Using Deionized Water and Seawater at 150ºF.

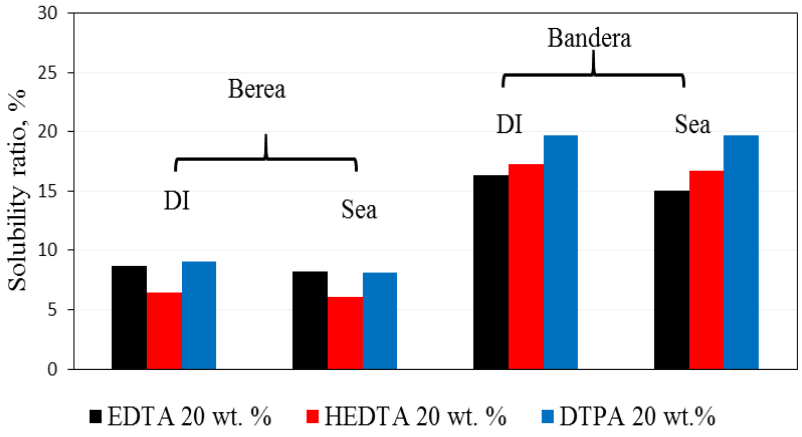


Figure 24 Solubility of Berea and Bandera in 20 wt. % HEDTA, EDTA and DTPA Solutions at pH of 11 Diluted Using Deionized Water and Seawater at 150ºF.

4.3.4 Effect of Adding Potassium Carbonate at 150ºF

Adding potassium carbonate to HEDT, EDTA and DTPA enhanced the solubility ratio of Berea and Bandera sandstone. The catalyst works to increase the amount of chelated cations. Chlorite and kaolinite have almost the same surface area. However, chelation

agents have higher stability constants with ferric cations (in chlorite) than aluminum (in kaolinite). As a result of that, adding the catalyst to the chelating agent will increase the solubility by capturing more ferric cations.

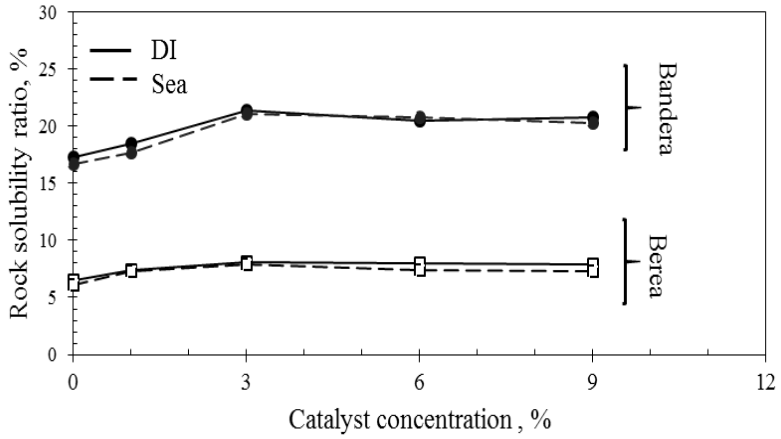


Figure 25 Solubility of Berea and Bandera in 20 wt. % HEDTA Solutions at pH of 11 with Different Concentrations of K_2CO_3 Diluted Using Deionized Water and Seawater at 150ºF.

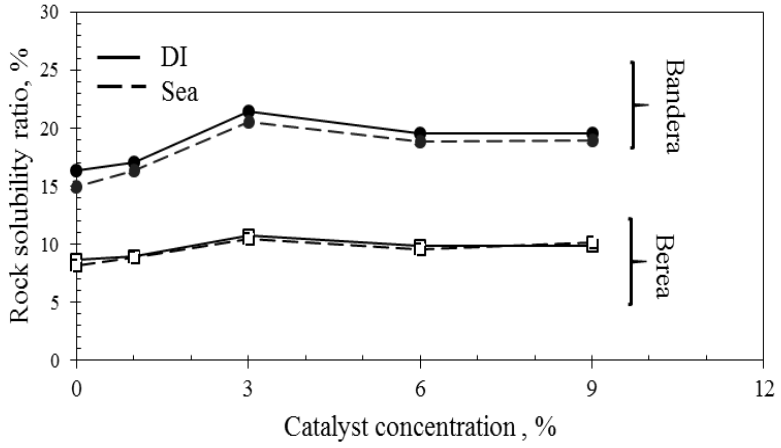


Figure 26 Solubility of Berea and Bandera in 20 Wt. % EDTA Solutions at pH of 11 with Different Concentrations of K_2CO_3 Diluted Using Deionized Water and Seawater at 150ºF.

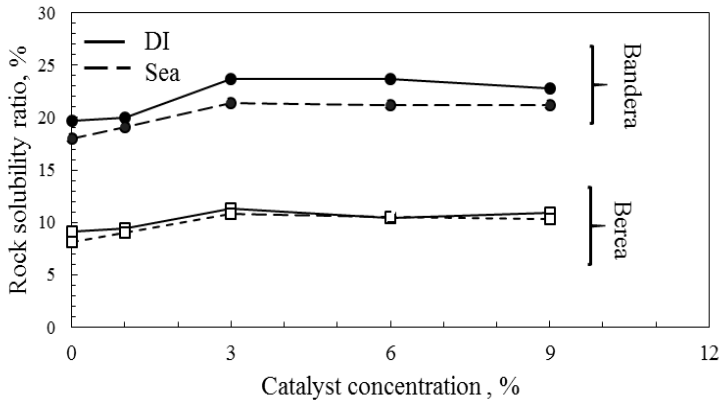


Figure 27 Solubility of Berea and Bandera in 20 wt. % DTPA Solutions at pH of 11 with Different Concentrations of K_2CO_3 Diluted Using Deionized Water and Seawater At 150ºF.

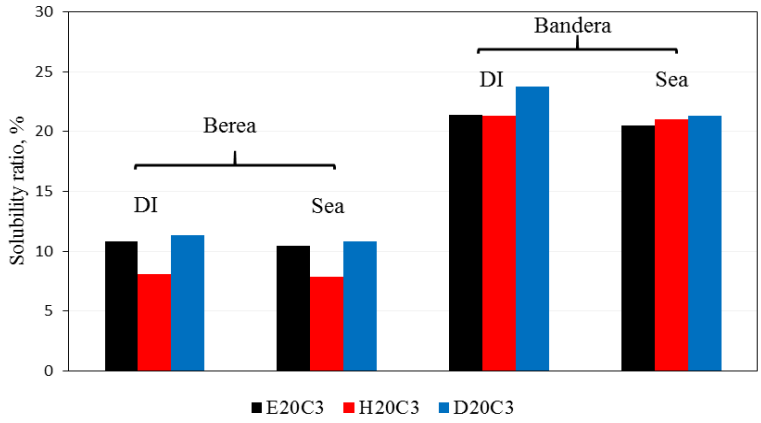


Figure 28 Solubility of Berea and Bandera in 20 Wt. % DTPA Solutions at pH of 11 with 3 wt. % of K_2CO_3 Diluted Using Deionized Water and Seawater at 150ºF.

4.3.5 Core Flooding

Core flooding experiments were performed using Bandera sandstone cores samples to assess the efficiency of the new formulated fluids. The length of all core samples used was 2 in. and the diameter was 1.5 in. The volume injected was 6 pore volumes in all the experiments at 5 cm^3/min flow rate and 250ºF. **Table 12** summarizes the four core flooding experiments.

Figure 29 shows the results of core flooding experiments using DTPA chelating agent. In the first core flooding experiment, 20 wt. % DTPA diluted with deionized water (D20-DI) was used. The injection of 6 pore volume of D20-DI solution into the Bandera core enhanced the permeability from an initial value of 8.75 md to a final permeability of 11 mD. The permeability enhancement ratio ($K_{final}/K_{initial}$) was 1.26. Adding 3 wt. % potassium carbonate catalyst to the solution (D20-C3-DI) raised the permeability ration to 1.33, therefore, the catalyst added 7% enhancement in the permeability when added to DTPA diluted with deionized water.

Similar trend was obtained for DTPA when it was diluted with seawater. The permeability ratio for the 20 wt. % DTPA diluted with seawater was 1.33 and this was more than that obtained for DTPA diluted with deionized water. This can be attributed to the help of seawater in DTPA solution in stabilizing clay minerals in the core (Bandera sandstone contains 10 wt. % illite, 3 wt. % kaolinite and 1 wt. % chlorite). The catalyst addition to the DTPA diluted with seawater yielded also 7% extra increase in the permeability and the permeability ratio increased from 1.33 to 1.40 after adding the catalyst. The role of seawater in DTPA solutions is very clear in Bandera sandstone cores.

Seawater (high salinity) will stabilize the clays (14% in Bandera) and allow more ion exchange between the DTPA and rock surface. Kaolinite has low cation-exchange capacity (Civan 2007), therefore, its reaction with chelating agents is very slow. Adding the potassium carbonate to DTPA/seawater based solutions will accelerate the ion exchange mechanism and enable DTPA to chelate more Al^{3+} from kaolinite. Potassium carbonate releases the potassium ions and carbonate group will be free in the solution.

Consequently, K^+ ions from the catalyst will reduce the illite expansion phenomena and prevent the damage. Chlorite has huge surface area (approximately 100 m^2/gm) and is very sensitive to acids (Civan 2007). Chelating agents are compatible with chlorite and they can capture Fe^{3+} to prevent further reactions. Kaolinite and chlorite has high surface area. However, chlorite will be attacked firstly because low ion exchange of kaolinite and high affinity of DTPA to ferric ions.

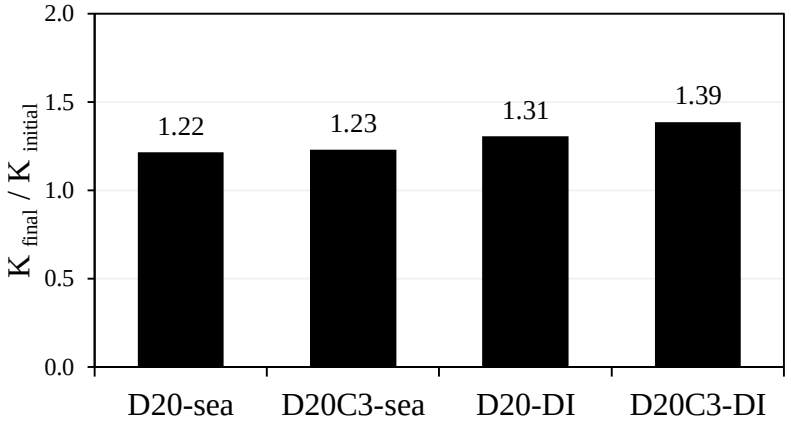


Figure 29 Comparison between Different DTPA Solutions (at pH=11) In Stimulating Bandera Gray Cores.

The normalized pressure drop (pressure drop / initial pressure drop) of the treated cores indicates that the new formulation (DTPA/catalyst) was compatible with the Bandera cores, **Figure 30**. The chelating agent was able to capture caions such as calcium, ferric, and magnesium from the cores and this increased the viscosity of the solutions and the pressure will increase (Mahmoud et al. 2011b, 2011c). The pressure drop inside the cores increased as a result of the complexation process and viscosity growth then the pressure drop stabilizes when no further reaction occurs inside the core.

Table 12 Stimulation of Bandera Sandstone Samples Using 20 wt. % DTPA (at pH = 11) Injected at 5 cm^3/min at Temperature of 250ºF.

Parameter	Core number			
	BN1	BN2	BN3	BN4
Porosity, %	18	18.85	17.03	17.3
Acid type	D20-sea	D20C3-sea	D20-DI	D20C3-DI
Initial permeability, mD	7	8.7	8.75	9
Final permeability, mD	9	12.2	11	12

Previous work on Bandera sandstone cores using mud acid showed continuous increase in the pressure drop and reduction in the final core permeability indicating damage due to fines migration and precipitation (Mahmoud et al. 2015).

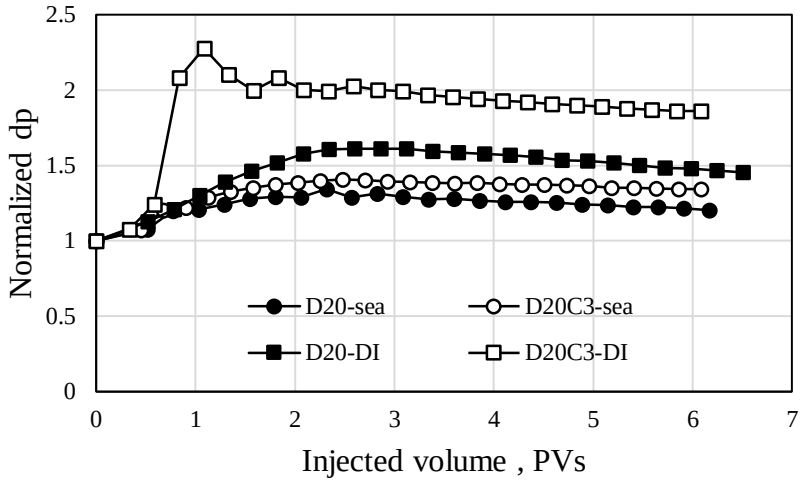


Figure 30 Normalized Differential Pressure For Bandera Cores Acidized With 6 PV Of DTPA Solutions Diluted Using Deionized Water With And Without Catalyst at pH Of 11, Injection Rate 5 cm^3/min And Temperature 250ºF.

4.4. Conclusions

In this part new formulation for sandstone acidizing based on chelating agents and catalyst was developed. The solubility and core flooding experiments proved the efficiency of the new formulation in treating sandstone cores. The following conclusions that can be drawn:

1. DTPA, EDTA, and HEDTA at pH of 11 were found to be compatible with seawater and no precipitations were detected.
2. The best solubility ratio was obtained at optimum concentration of 20 wt. % of chelating agents at pH of 11 and at optimum concentration of 3 wt. % of the potassium carbonate catalyst.
3. Increasing the temperature enhanced the solubility sandstone rocks in chelating agents.
4. Core flooding experiments showed compatibility of the new formulated seawater based fluid with Bandera sandstone cores. The permeability enhancement reached 40% for 20 wt. % DTPA combined with 3 wt. % of the catalyst at 250^{o}F and injection rate 5 cm^{3}/min.

CHAPTER 5

SANDSTONE ACIDIZING USING NOVEL TECHNIQUE

5.1 Introduction

With the current expansion in offshore operations, there is a real need to reduce the high cost of stimulating sandstone formations by using seawater. For this purpose, scientists developed compatible seawater based acids. However, the main problem of using seawater based fluids is the calcium sulfate precipitation. Acids such as conventional mud acid, hydrofluoric acid and organic acids were used to reduce the skin and remove the damage in sandstone formations to enhance the productivity of the well. Recently, researchers introduced chelating agents as stimulation fluids for sandstone reservoirs.

In this part of the research, core flooding tests were done to determine the effectiveness of the new formulations as a stand-alone stimulation fluids for Berea and Bandera sandstones. Diethylene triamine Penta-acetic acid (DTPA) and Ethylene diamine tetra-acetic acid (EDTA) chelating agents at high pH were used. Induced coupled plasma (ICP) analysis was used to understand the working mechanism of the catalyst. The effects of injection rate, temperature, injected volume of acid and core length on the permeability of the cores were studied.

5.2 Experiments

5.2.1 Materials

Berea and Bandera cores with lengths 2 and 6 inches and diameter 1.5 inches were used. 3 wt. % KCl was used as brine. EDTA and DTPA chelating agent at pH of 11 with initial concentration 40 wt. % were used for core flooding experiments. Potassium carbonate was added to the chelating agents as catalyst.

5.2.2 Core Saturation

2-6 inches Bandera gray and Berea Gray cores were prepared. The cores were dried at 65^{o}C for one day and the dry weight was measured. 3 wt. % KCl brine was used to saturate them in order to measure the porosity.

At first, to make sure that there is no air bubbles inside the cores vacuum pumping was applied for two hours. Then the cores were saturated under vacuum pressure until the level of the fluid kept constant in the flask. Then a pump was used to inject the KCl brine into the saturation cell to make 2500 psi pressure inside the cell. After that, the pressure monitored for 24 hours until it stabilized. Finally, all samples were weighed wet. Porosity was calculated using the weight difference method.

5.2.3 Core Flooding Tests

The brine and the acids were transferred into the accumulators inside the core flooding system. The core sample was loaded in the core holder. The core and the fluids were heated for 6 hours until the temperature stabilized at the target value. 2000 psi Overburden pressure was applied to the core sample and the back pressure was 1000 psi

for all the experiments. These pressures were increased gradually with maximum difference between them to be about 500 psi until the specific values were got. 3 wt. % KCl brine used for pre-flush stage and post flush to measure the initial and final permeability of the core after treatment with the main acid. At first, the core was pre-flushed with the brine, the main acid was injected and then post flushed with 3 wt. % KCl brine.

5.3 Results and Discussion

5.3.1 Stimulating Sandstone Cores Using High pH Chelating Agents

EDTA and DTPA were used to acidize Berea 2 inches length cores and 1.5 inches diameter. The best increase in permeability percentage for Gray Berea cores was observed using 20 wt. % EDTA combined with 3 wt. % potassium carbonate diluted by deionized water, and it was 36 % (**Figure 31**).

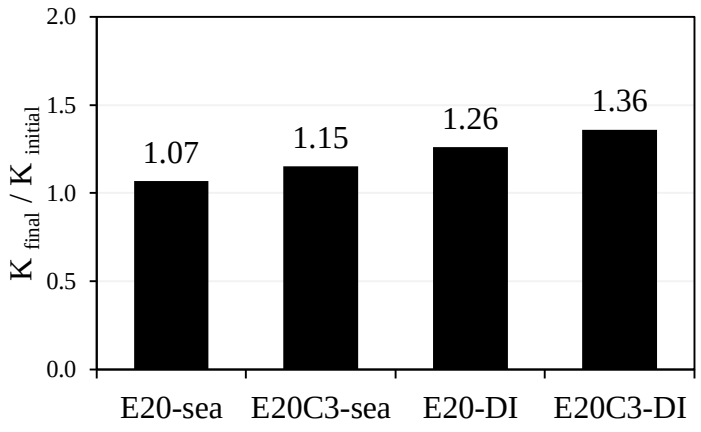


Figure 31 Permeability Improvement Ratio for Berea Cores Stimulated Using EDTA Solutions (pH = 11) at 250°F Injection Rate 5 cm^3/min.

In contrast to Bandera Gray, using seawater did not show good results in case of Gray Berea cores. However, no damage was detected. **Figure 32** indicates that EDTA 20 wt. % was able to enhance the permeability of Bandera Gray cores after injecting 6 pore volumes. EDTA 20 wt. % diluted using deionized water showed very low increment in permeability ratio. On the other hand, using seawater to dilute the solution gave better enhancement up to 13 %. Then after stimulating Bandera cores after adding the potassium carbonate to the solutions, better results were obtained. There was 8 % increase in case of deionized water. While for seawater the percentage raised up to 1.27. The chelating of Ca^{2+}, Mg^{2+} and Fe^{3+} causes increase in differential pressure due to viscosity increase by complexation of these cations (Mahmoud et al., 2010). On the other hand, using DTPA to stimulate Berea and Bandera sandstones showed better results than EDTA.

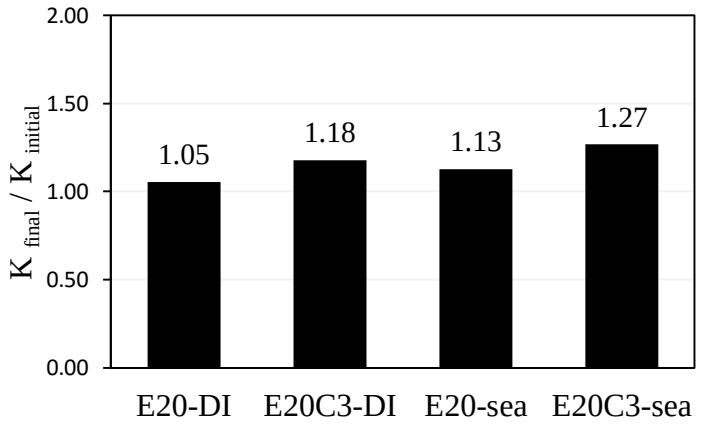


Figure 32 Permeability Improvement Ratio of Bandera Gray Cores Stimulated Using EDTA (pH = 11) Solutions at 250ºF and Injection Rate 5 cm^3/min.

For Berea cores (**Figure 33**) DTPA diluted using deionized water with 3 wt. % potassium carbonate enhanced the permeability ratio to 39 %. Using seawater with the catalyst did not enhance the ratio.

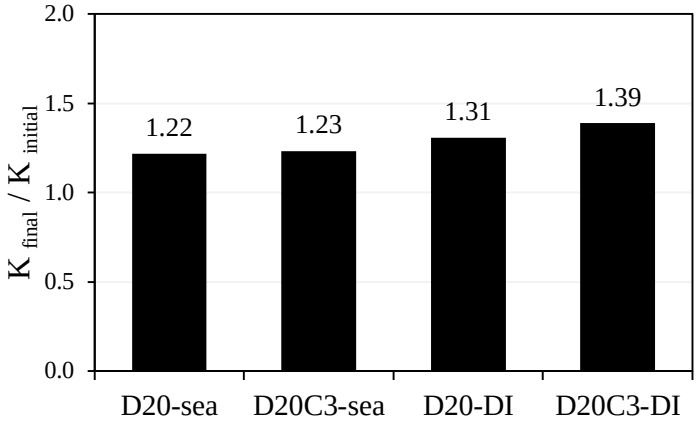


Figure 33 Permeability Improvement Ratio of Berea Gray Cores Treated Using DTPA Solutions (pH = 11) at 250ºF and Injection Rate 5 cm³/min.

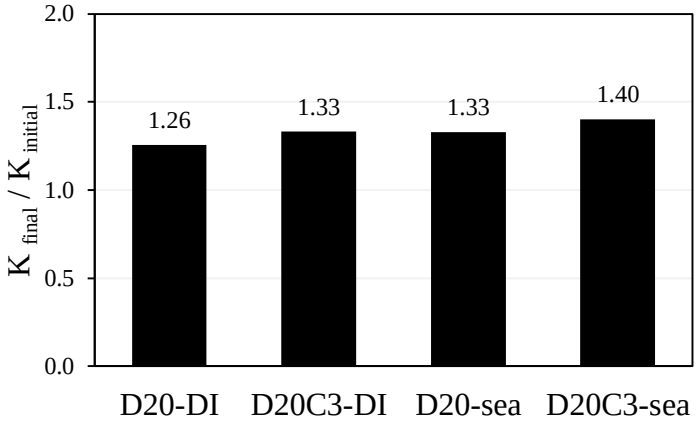


Figure 34 Permeability Ratio of Bandera Gray Cores Stimulated Using DTPA Solutions (pH = 11) at 250ºF and Injection Rate 5 cm³/min.

The normalized differential pressure of the treated cores showed that the DTPA solutions diluted using deionized water and seawater at pH of 11 are compatible with Berea and Bandera sandstones (**Figure 35** and **Figure 36)**

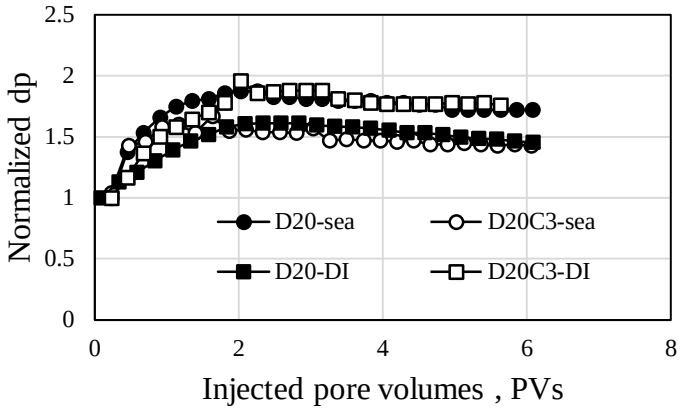


Figure 35 Normalized Differential Pressure across Berea Gray Cores Stimulated Using DTPA Solutions (pH = 11) at 250°F and Injection Rate 5 cm³/min.

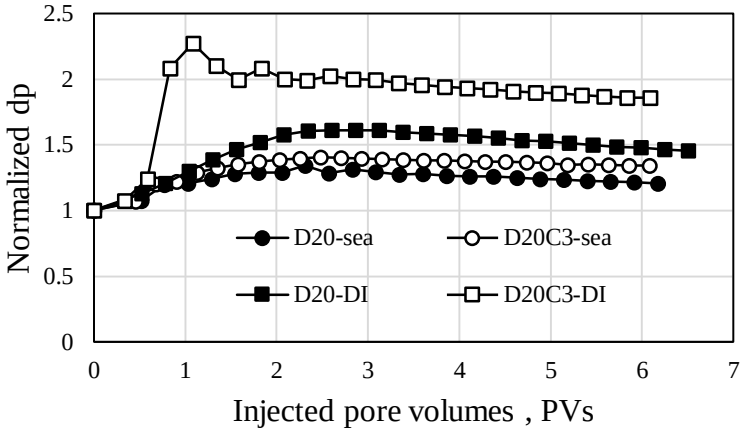


Figure 36 Normalized Differential Pressure across Bandera Gray Cores Stimulated Using DTPA Solutions (pH = 11) at 250°F and Injection Rate 5 cm³/min.

5.3.2 ICP Analysis

The collected effluents during the core flooding experiments were analyzed using ICP to understand of the working mechanism of adding the potassium carbonate catalyst to the chelating agents solutions. **Figure 37** shows the cumulative amount of dissolved calcium, magnesium, ferric and aluminum cations after treating Bandera sandstone core samples with 6 PVs of 20 wt. % DTPA at pH of 11 diluted using seawater before and after adding the catalyst and compares it with EDTA solutions. It can be clearly observed that adding potassium carbonate the chelating agents increased the amount of chelated cations. DTPA has higher stability constants with calcium, magnesium, ferric and aluminum than EDTA.

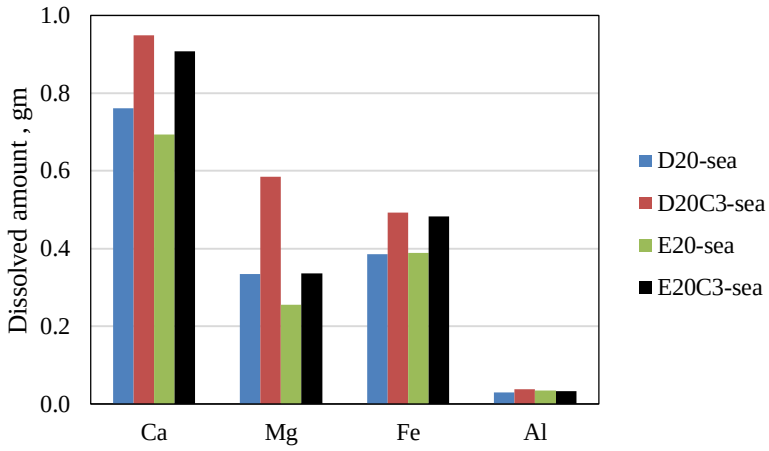


Figure 37 ICP Analysis of Effluents after Injecting 6 PVs of DTPA and EDTA Solutions Before and After Adding the Catalyst at pH of 11 Diluted Using Seawater into Bandera Cores at Injection Rate of 5 cm^3/min and Temperature of 250°F.

For the Bandera samples treated using DTPA solutions diluted using deionized water (**Figure 38**) the chelated amount of cations was higher than the case of seawater. However, the better performance could be attributed to the assistance of seawater in stabilizing clays. Himes et al., 1991 reported two main mechanisms of formation damage

when the clay is interacted using low salinity solutions. Clay swelling when the water been adsorbed into the clay crystalline structure. Moreover, plugging of the pore throats as a result of fines migration. To avoid these damage mechanisms, saline solutions generally used to stabilize the clay.

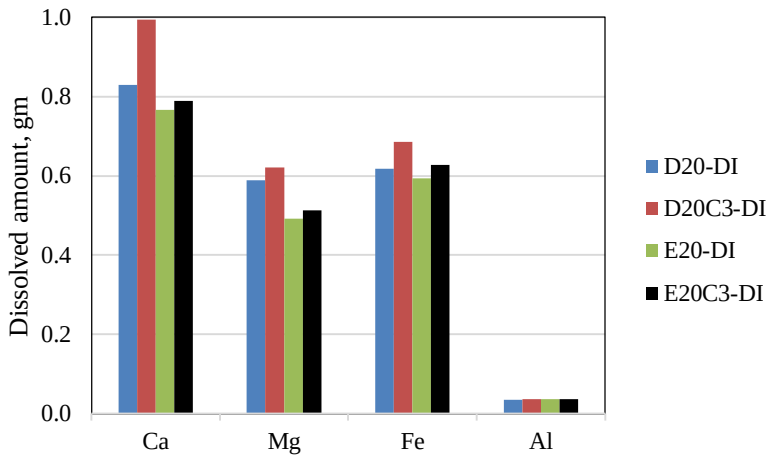


Figure 38 ICP Analysis of Effluents after Injecting 6 PVs of DTPA and EDTA Solutions Before and After Adding the Catalyst at pH of 11 Diluted Using Deionized Water into Bandera Cores at Injection Rate of 5 cm^3/min and temperature of 250°F.

The chelated amount of calcium, magnesium, ferric and aluminum was lower in Berea case than Bandera because Berea sandstone has low amount of calcite and dolomite. Moreover, the role of clay stabilization of seawater was not very effective because the low percent of clays. **Figure 39** shows the chelated cations from Berea cores using DTPA and EDTA solutions diluted using seawater. Using the solutions of chelating agents diluted with deionized water to treat Berea core (**Figure 40**) chelated higher amount of cations.

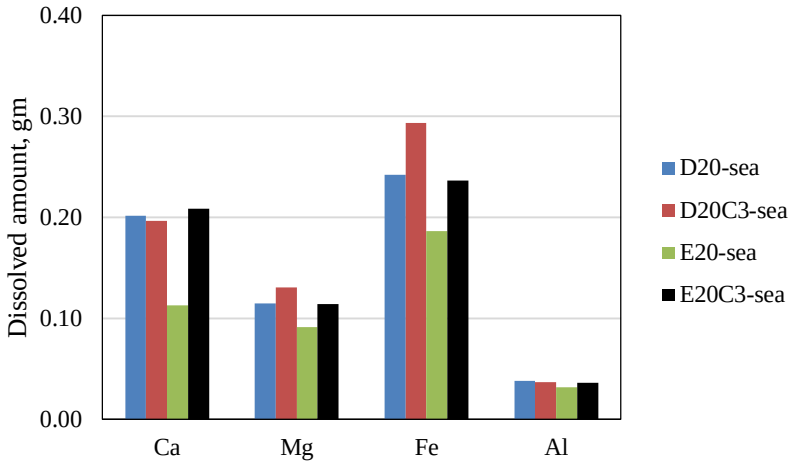


Figure 39 ICP Analysis of Effluents after Injecting 6 PVs of DTPA and EDTA Solutions Before and after Adding the Catalyst at pH of 11 Diluted Using Seawater into Berea Cores at Injection Rate of 5 cm^3/min and Temperature of 250ºF.

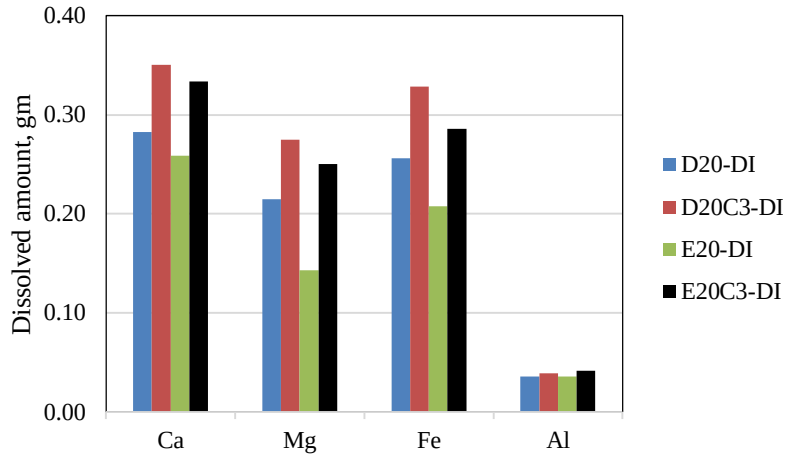


Figure 40 ICP Analysis of Effluents after Injecting 6 PVs of DTPA and EDTA Solutions before and after Adding the Catalyst at pH Of 11 Diluted Using Deionized Water into Berea Cores at Injection Rate of 5 cm^3/min and Temperature of 250ºF.

5.3.3 Effect of Injection Rate on Permeability Ratio

The acid injection rate during stimulation job must be less than the formation fracturing pressure. Decreasing the injection rate means increasing the reaction time between the acid and rock minerals. It provides more time for the weak acids (chelating agents) to

react with the rock minerals which gives better permeability enhancement. However, in most cases economics determine the optimum acid injection rate. Injected pore volume was kept constant at 6 pore volumes. Two injection rates were used 5 and 1 cm^3/min.

The core flooding experiments showed that lower injection rate increased the permeability ratio. Reducing the acid injection rate from 5 to 1 cm^3/min raised the permeability ratio to more than double using DTPA in Berea sample and 1.69 for Bandera core. Using EDTA increased the K_{final} / $K_{initial}$ to 1.76 and 1.45 for Berea and Bandera respectively (**Figure 41**).

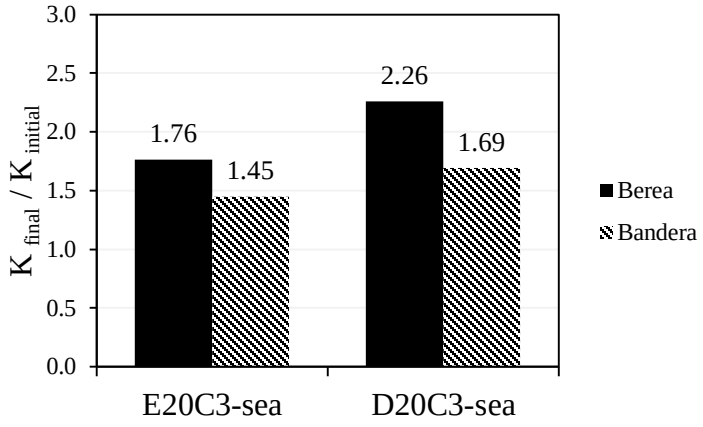


Figure 41 Effect of Acid Injection Rate on Permeability Improvement Ratio of Bandera and Berea Cores Stimulated Using EDTA and DTPA Solutions (pH = 11) at 250°F Using Injection Rate of 1 cm^3/min.

The injected acids EDTA and DTPA both were compatible with Bandera and Berea sandstones because no fines migration was detected in the collected samples. Moreover, the pressure profile during the injection of the chelating agents did not show any disturbance mean that they were compatible with clays inside the cores.

5.3.4 Effect of Temperature on Permeability Ratio

Generally, increasing temperature will accelerate the reaction of the acids with rock minerals. Chelating agents showed good stability at high temperatures (Sokhanvarian et al., 2012). Core flooding tests were done at two different temperatures 150 and 250°F at injection rate of 5 cm^3/min.

Raising the temperature increases the amount of chelated cations and hence the permeability after acidizing. At 150°F, both EDTA and DTPA showed poor permeability improvement ratio around 10 % for Berea and Bandera cores (**Figure 42**).

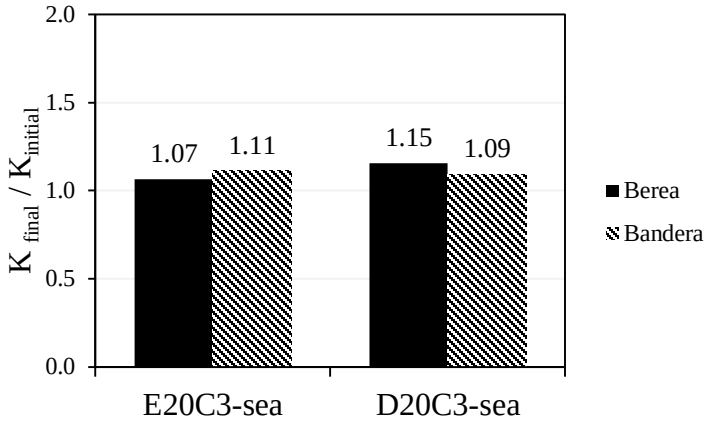


Figure 42 Permeability Improvement Ratio of Berea and Bandera Sandstones Stimulated Using EDTA and DTPA Solutions (pH = 11) at 150°F at Injection Rate 5 cm^3/min.

Increasing the temperature up to 250°F resulted in 27 % increase in permeability ratio when EDTA used to treat Bandera sandstone. The ratio growth to 40 % after using DTPA. For Berea only 8 % was noticed as effect of temperature at 5 cm^3/min.

5.3.5 Effect of Injected Acid Volume on the Permeability Ratio

When the injected volume of the acid Increased, the dissolvable minerals will expose to additional amount of acid. Consequently, the permeability is expected to increase. **Figure 43** and **Figure 44** show permeability increase after raising the injected volume of EDTA and DTPA to 10 pore volumes. After injecting 10 PV of EDTA in Berea cores the permeability ratio increased to 40 %. For Bandera the percent improved to 32 %. Using DTPA showed better results 40 % for Berea and 44 % for Bandera.

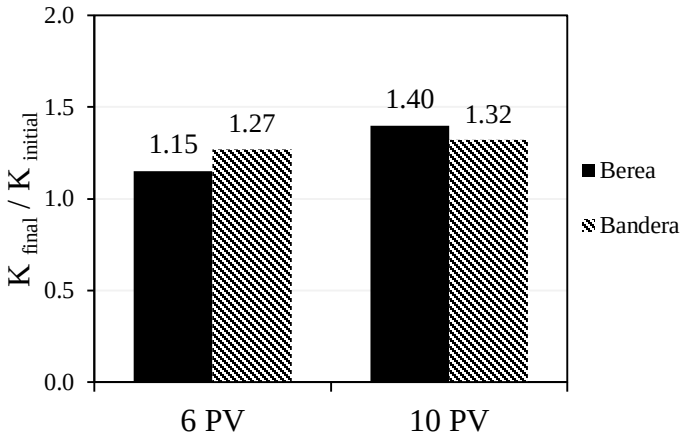


Figure 43 Permeability Improvement Ratio of Berea and Bandera Sandstones after Injecting 6 and 10 Pore Volumes of EDTA Solution (pH = 11) at 250ºF at Injection Rate 5 cm^3/min.

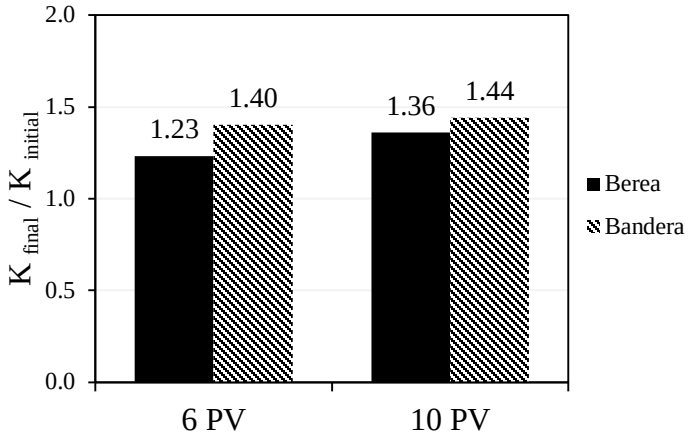


Figure 44 Permeability Improvement Ratio of Berea and Bandera Sandstones after Injecting 6 and 10 Pore Volumes of DTPA Solution (pH = 11) at 250ºF at Injection Rate 5 cm^3/min.

5.3.6 Effect of Core Length on the Permeability Ratio

6 inches cores were used to compare to the performance of the new fluids to 2 inches cores. Increasing the core length can give clear idea about the performance of the acid because the injected pore volume will increase. **Figure 45** shows permeability improvement of Bandera and Berea samples.

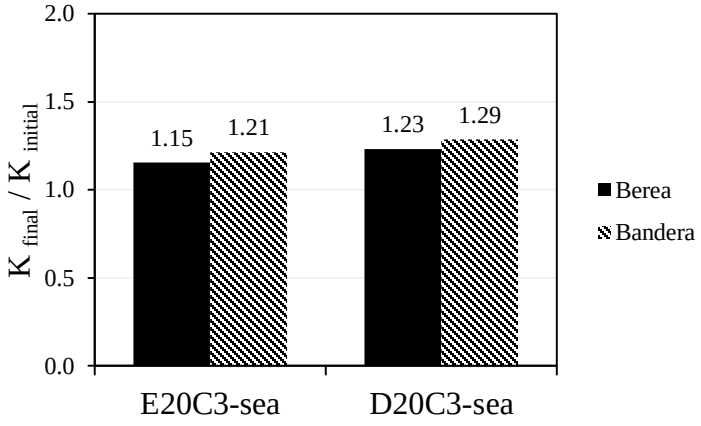


Figure 45 Permeability Improvement Ratio of Berea and Bandera Sandstones 6 Inches Cores Stimulated Using EDTA and DTPA Solutions (pH = 11) at 250ºF and Injection Rate of 5 cm^3/min.

It was around 30 % using DTPA and 21 % when EDTA was injected. For Berea the permeability enhancement was less, 23 % using DTPA and 15 % using EDTA.

5.4 Conclusions

The influence of adding potassium carbonate catalyst on the performance of EDTA and DTPA was investigated. Based on core flooding experiments, the following conclusions can be summarized:

1. DTPA and EDTA found to compatible with seawater and no precipitations were detected.
2. The new formulated fluids improved the permeability of Bandera and Berea sandstones.
3. ICP analysis showed that adding 3 wt. % of potassium carbonate to DTPA and EDTA increased the chelated amount of cations.
4. Decreasing the acid injection rate improved the permeability of the cores because it provides more time to the acid to react with rock minerals.
5. Raising the temperature enhanced the reaction rate and consequently the permeability.
6. Increasing the injected pore volume of the acid increased the permeability ratio.
7. Using long cores (6 inches) showed the performance of the new formulations better than short cores (2 inches).

CHAPTER 6

EFFECT OF NOVEL CHELATING AGENT SEAWATER BASED SYSTEM ON THE INTEGRITY OF SANDSTONE ROCKS.

6.1 Introduction

Generally the objective of sandstone acidizing is to reduce the skin around the well bore. This process could affect the stability of the formation and may decrease the efficiency of the stimulation job. One of the main problems related to rock integrity is sand production. Sand causes erosion of surface and downhole equipment. The objective of this chapter is to use mechanical properties estimated based on acoustic measurements to address the impact of the novel acid systems on the integrity of Bandera and Berea cores after stimulation.

DTPA and EDTA (ethylene di-amine tetra-acetic acid) chelating agents at high pH diluted with seawater combined with potassium carbonate were used to acidize Bandera and Berea sandstone cores. Core flooding system was used to acidize the sandstone samples. Non-destructive tests were conducted to evaluate the effect of injected pore volumes of the acid on the rock integrity. The samples were scanned using Computed

Tomography (CT) scan to detect any precipitations after using the seawater based chelating agents.

6.2 Rock Mechanical Properties

The Primary waves (p-waves) are longitudinal waves which transfer along the same direction of the medium displacement. P-wave can travel through solids and fluids. Whereas the shear waves (secondary waves-because they are slower than p-waves-) (s-waves) are move perpendicularly to the wave direction and travel through solids only. The velocities of both s-wave and p-wave are useful to address the wellbore stability by monitoring the values of elastic moduli (Fjar et al. (2008)).

6.2.1 Elastic Moduli

This group of moduli includes Young's modulus, bulk modulus, Poisson's ratio and shear stress. These moduli are used to measure the stiffness of the acidized cores. In another words they give indications of what happened after treatment by monitoring the velocity of p-waves and s-waves. Young's modulus is a ratio of stress to strain along an axis and it is related to core stiffness.

$$E = \rho v_p^2 \frac{3v_p^2 - 4v_s^2}{v_p^2 - v_s^2} \tag{6.1}$$

Poisson's ratio reflects the rock compressibility and can be defined as an amount of lateral expansion relative to longitudinal contraction.

$$v = \frac{v_p^2 - 2v_s^2}{2(v_p^2 - v_s^2)} \tag{6.2}$$

Shear modulus is the resistivity of the core against the shear deformation.

$$G = \rho v_s^2 \tag{6.3}$$

Bulk modulus known as the inverse of the compressibility and it is the resistance of the sample to hydrostatic compression.

$$K = \rho v_p^2 - \frac{4}{3}\rho v_s^2 \tag{6.4}$$

Clegg (2007) pointed out that many factors may cause sand production such as degree of consolidation. Compressive strength is a mechanical characteristic of rock that is related to the degree of consolidation. This is a clue of the strength of the sand grains and how they are bound together. The compressive strength of poorly consolidated sandstone formations is less than 1,000 psi (Clegg 2007).

6.3 Experiments Procedures

6.3.1 Materials

Berea and Bandera 2 inches length and 1.5 inches diameter cores were used during the experiments. 3 wt. % KCl was used to saturate the cores and as brine for pre-flush and post-flush stage in the core flooding runs. 20 wt. % EDTA and DTPA at pH of 11 diluted using seawater combined with 3 wt. % of potassium carbonate were used to acidize the core samples.

6.3.2 Experiments Set Up

At first, 2 inches Bandera and Berea cores were dried at 65^{o}C for 24 hours and the dry weight was measured. The weight difference method was used to estimate the porosity after saturating the cores by 3 wt. % KCl. The cores were CT-scanned after saturation.

Acoustic measurements were used to measure the velocity of p-waves and s-waves to calculate the moduli and evaluate the rock integrity. Berea and Bandera cores were loaded to a sleeve to apply overburden pressure on them. Manual pump was connected the acoustic system to control the confining pressure. Overburden pressure was increased gradually from 3, 5.5, and 8.3 to 10 MPa. At each pressure the acoustic system was used to capture the velocity of p-wave and s-wave. Then the pressure was decreased again in the same sequence.

Then core flood system was used to inject the acids into the cores. The overburden pressure was 2000 psi and the back pressure was 1000 psi. The injection rate was 5 cm^3/min and the temperature 250^{o}F for all the experiments. 3 wt. % KCl brine was used for pre-flush stage and post flush to measure the permeability of the core before and after the treatment with the main acid. 6 PVs of the acid were initially injected. The final permeability after treatment was estimated, the cores were CT-scanned and the acoustic measurements were done again. The same steps repeated after injecting 10 pore volumes.

6.4 Results and Discussion

6.4.1 Effect of Injected Pore Volumes on The Permeability Ratio

Increasing the injected pore volumes of the acid means more acid will contact the minerals inside the cores. As a result of dissolving carbonates and clays the permeability is expected to raise. For Berea sandstone, the permeability improved by 15 % after injecting 6 PVs of 20 wt. % EDTA acid (pH of 11) at injection rate of 5 cm^3/min at temperature 250°F. Increasing the injected pore volumes to 10 PVs increased the permeability ratio to 40 %. Bandera cores treated using EDTA solution showed 28 % improvement in permeability ratio after injecting 6 PVs. After increasing the injected pore volume to 10 PVs, the permeability ratio grow to 32 % (**Figure 46**).

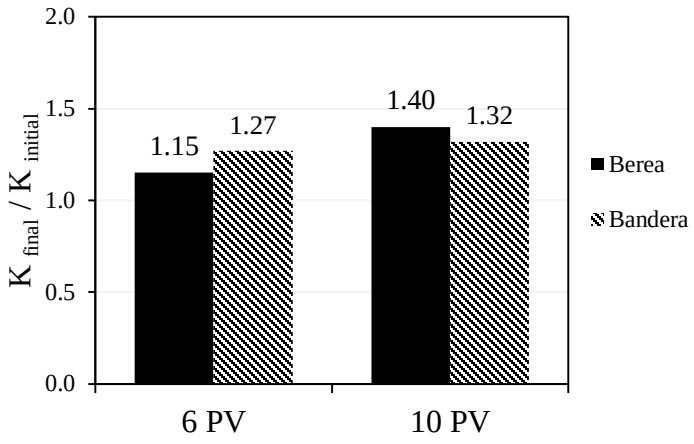


Figure 46 Permeability Improvement Ratio of Berea and Bandera Sandstones after Injecting 6 and 10 Pore Volumes of EDTA Solution (pH = 11) at 250°F at Injection Rate 5 cm^3/min.

On the other hand, using DTPA at the same conditions to acidize Berea samples showed 23 % and 36 % enhancement in the permeability ratio to after injecting 6 PVs and 10 PVs respectively. For Bandera sandstone, using DTPA gave 40 % enhancement in

permeability ratio. After injecting 10 the percentage increased to 44 % (**Figure 47**). Table 3 shows the initial properties of the cores.

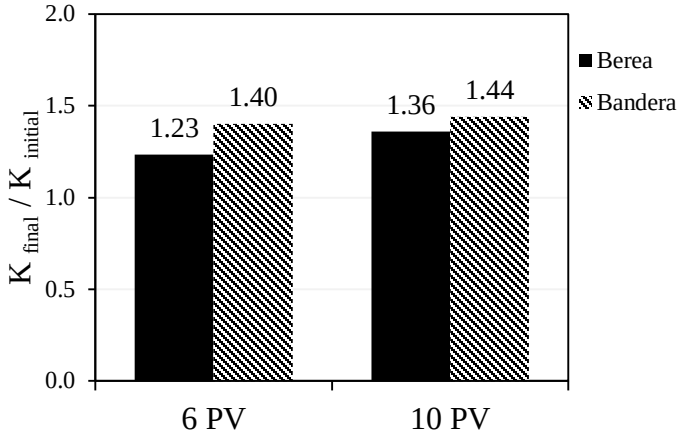


Figure 47 Permeability Improvement ratio of Berea and Bandera Sandstones after Injecting 6 and 10 Pore Volumes of DTPA Solution (pH = 11) at 250ºF at Injection Rate 5 cm³/min.

6.4.2 Effect of Injected Acid Volume on the Elastic Properties of Sandstone Cores

Elastic properties of the rock are useful indicators of the changes happened for the formation. Thus they are used to evaluate wellbore stability after acidizing jobs as well as to predict sanding problem in sandstone formations.

Figure 48 shows Young's moduli of sandstone cores after injecting 20 wt. % DTPA and EDTA acids (pH=11) after adding 3 wt. % of potassium carbonate catalyst diluted using seawater on. For Berea samples, insignificant reduction in Young's modulus was recorded after treating the cores with the two acids. In contrast, Young's modulus sharply decreased after injecting 6 pore volumes of 20 wt. % DTPA and EDTA for Bandera cores.

Table 13 Properties of Bandera and Berea Sandstone Cores.

Parameter	Samples			
Sample number	BR 1	BR 2	BN 1	BN 2
Rock type	Berea	Berea	Bandera	Bandera
Core length , in	1.95	2	1.85	2.05
Porosity , %	18.6	18.53	17.28	18.85
Initial permeability , mD	86.87	88.22	8.2	8.7
Acid type	E20C3-sea	D20C3-sea	E20C3-sea	D20C3-sea

The reduction in Bandera cores could be related to the amount of dissolved minerals. Bandera cores contain 16 % dolomite, calcium plagioclase and clays. Chelating agents can chelate magnesium, calcium and ferric which are higher in Bandera than Berea cores,

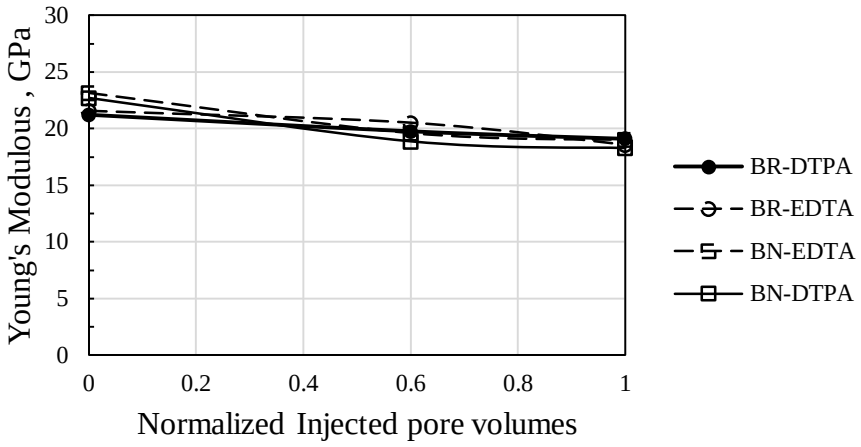


Figure 48 Effect of Injected Pore Volumes of EDTA and DTPA on the Young's Moduli of Berea and Bandera Cores.

Generally, when the injected pore volume increases Young's modulus declines indicating success of the treatment. The s-waves and p-waves transfers through the rock body. The velocity of these waves declined when the acid dissolved cementing minerals such as carbonates and clays. As a result of that, Young's modulus will decrease indicating the discontinuity of the pores as a result of dissolving cementing minerals and hence permeability enhancement. Bandera cores acidized with 20 wt. % DTPA combined with 3 wt.% potassium carbonate diluted using seawater showed the largest decrease in Young's modulus value as well as highest permeability enhancement after injecting 10 PVs.

Poisson's ratio showed little increase for the two types of sandstone after treatment (**Figure 49**). S-waves can transfers only through solids. Increasing Poisson's ratio means that amount of minerals inside the core decreased and replaced with the brine (3 wt. % KCl).

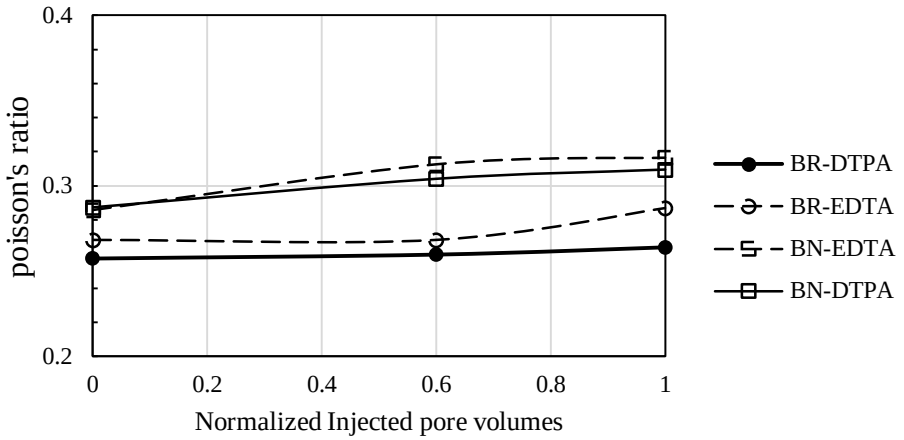


Figure 49 Effect of Injected Pore Volumes of EDTA and DTPA on the Poisson's Ratio of Berea and Bandera Cores.

Poisson's ratio cannot clearly reflect the enhancement of permeability because the increase is small. Increasing Poisson's ratio means increasing the compressibility of the cores.

Shear modulus directly proportional to the velocity of s-waves. Dissolving some minerals in sandstone cores such as carbonate and dolomite will decrease s-wave velocity because it can only travels through solids. Consequently, shear modulus will decrease as shown in **Figure 50.**

Bulk compressibility of the formation is related to the formation strength. Sand production and sand un-consolidation can be predicted early using the compressive strength of the formation. Berea and Bandera types are consolidated sandstones both have porosity around 20 % so the compaction strength of the grains is high.

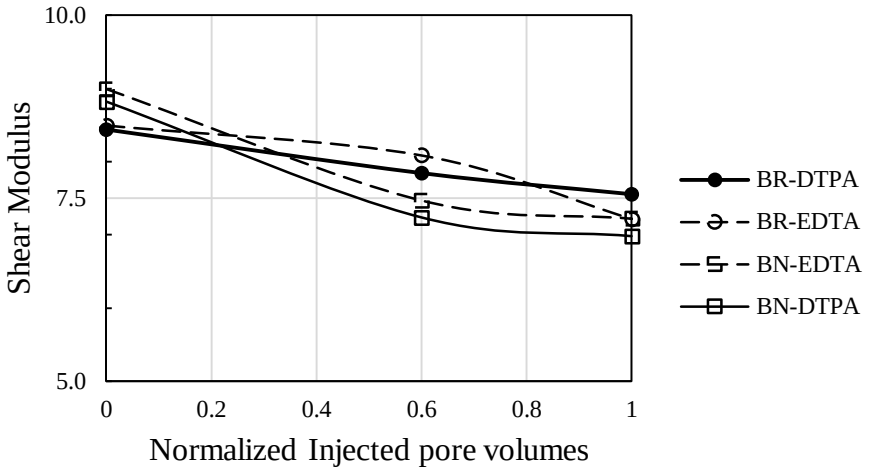


Figure 50 Effect of Injected Pore Volumes of EDTA and DTPA on the Bulk Moduli of Berea and Bandera Cores.

Table 14 summarizes the properties and velocities of Berea and Bandera core samples which were used to calculate the elastic moduli

6.4.3 Effect of The Injected Pore Volumes on The Average CT Number

Changes in average CT number of the cores reflects if there is perception inside the pores or not. For both Berea and Bandera samples the decrease in average CT-number indicates that there is no precipitation inside the cores. For Berea samples, the CT-number declined from 1730 to 1630 after injecting 10 PVs of DTPA fluid (**Table 15**). While for the sample treated using EDTA the CT-number dropped from 1725 to 1650 (**Table 16**). Bandera sandstone has higher CT-number than Berea which reflects its stiffness. Injecting 10 PVs of EDTA decreased the CT-number from 2000 to 1920 (**Table 17**) and for DTPA case the number declined to 1820 (**Table 18**).

Table 14 Properties of Berea and Bandera Core Samples Used to Calculate The Elastic Moduli (The Velocities Was Recorded at 5.5 MPa)

Property	Initial	6 PVs	10 PVs
BR 1			
Density, g/cm^3	2.21	2.18	2.16
Vp, m/s	3422	3326	3303
Vs, m/s	1956	1895	1870.5
BR 2			
Density, g/cm^3	2.25	2.24	2.20
Vp, m/s	3389	3374	3317
Vs, m/s	1907	1898.5	1813
BN 1			
Density, g/cm^3	2.35	2.33	2.32
Vp, m/s	3571	3427	3406
Vs, m/s	1955.5	1789	1764.5
BN 2			
Density, g/cm^3	2.31	2.28	2.28
Vp, m/s	3580	3356	3335
Vs, m/s	1955.5	1780.5	1751.5

Table 15 CT-number of Bandera Core before and after Injecting 20 wt. % DTPA Comebined with 3 wt. % K_2CO_3

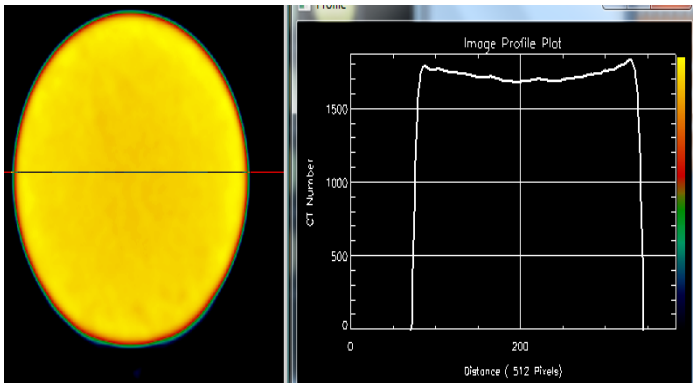
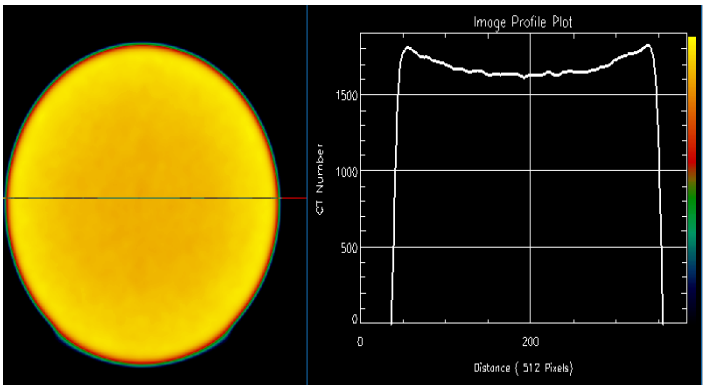
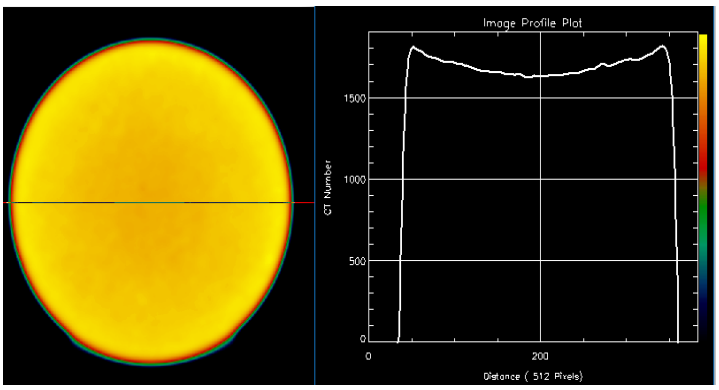
Slice	Average CT-number	Injected pore volume
	1730	Initial
	1650	6 PVs
	1630	10 PVs

Table 16 CT-number of Bandera Core before and after Injecting 20 wt. % EDTA Combined with 3 wt. % K_2CO_3

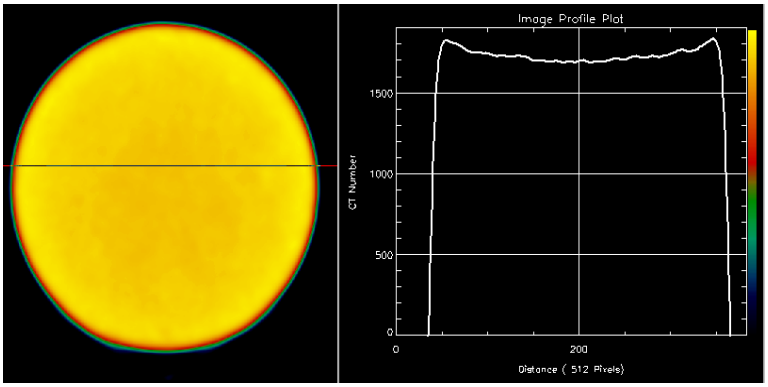
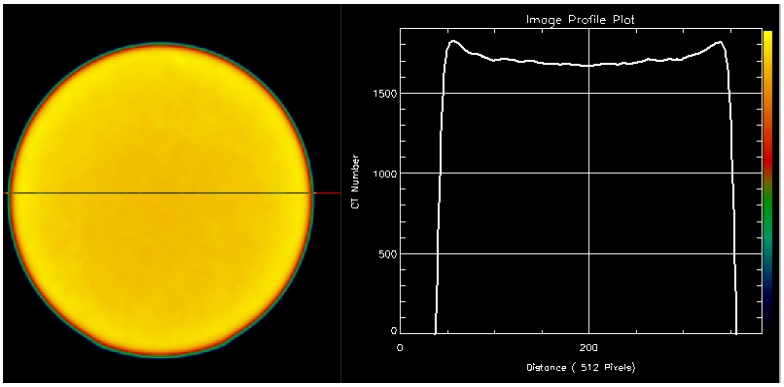
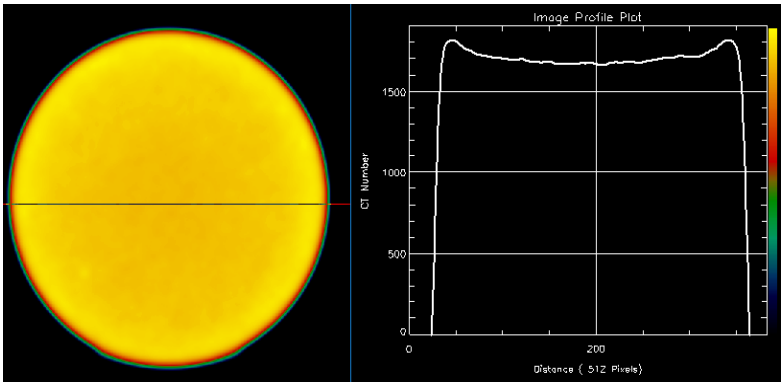
Slice	Average CT-number	Injected pore volume
	1725	Initial
	1680	6 PVs
	1650	10 PVs

Table 17 CT-number of Bandera Core before and after Injecting 20 wt. % EDTA Combined with 3 wt. % K_2CO_3

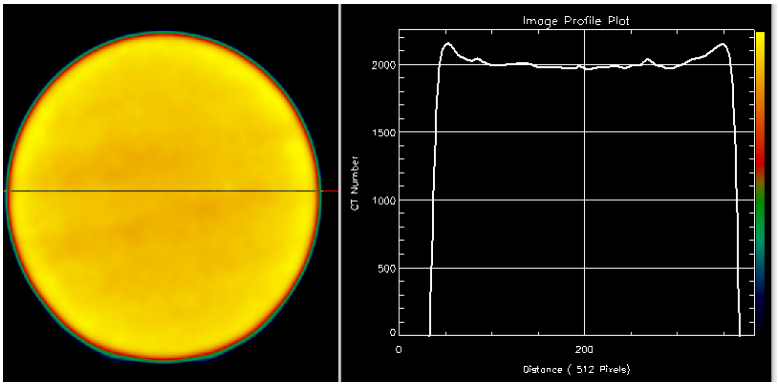
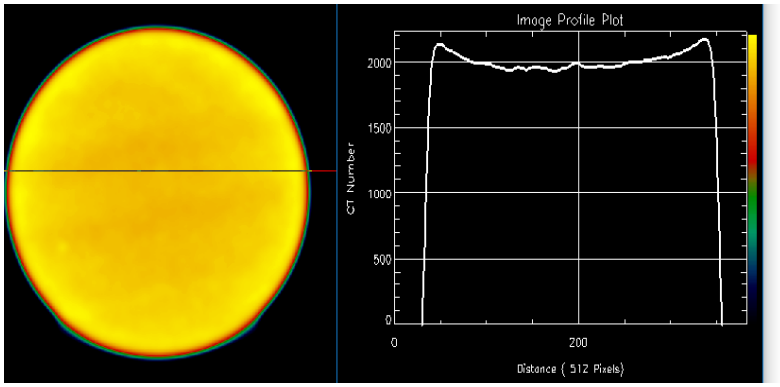
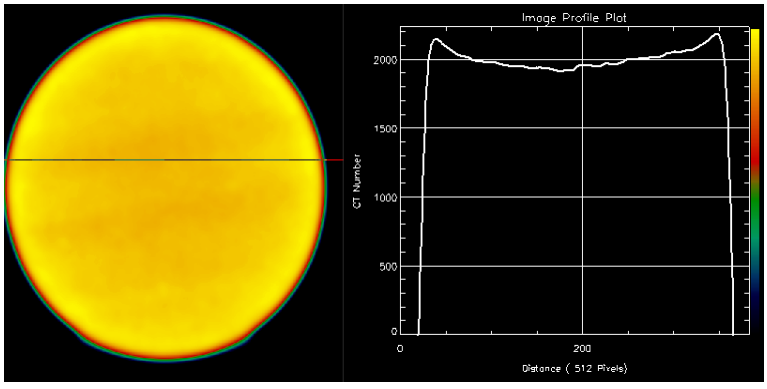
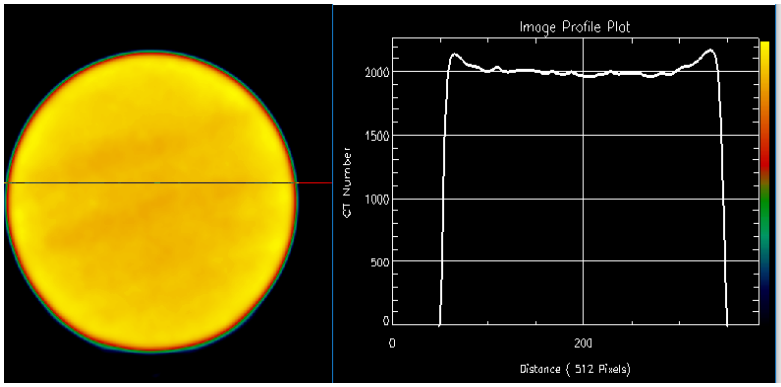
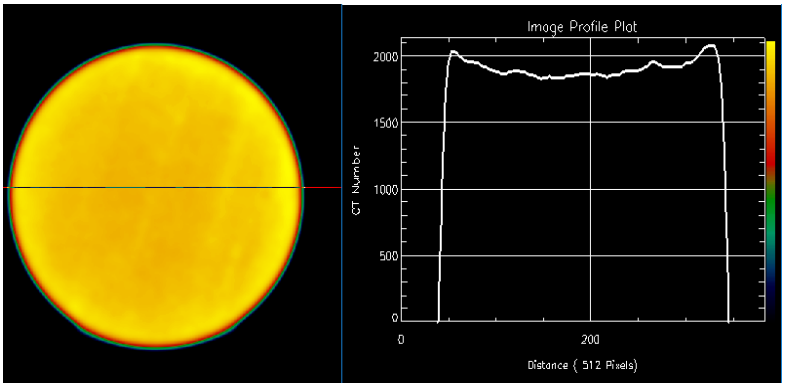
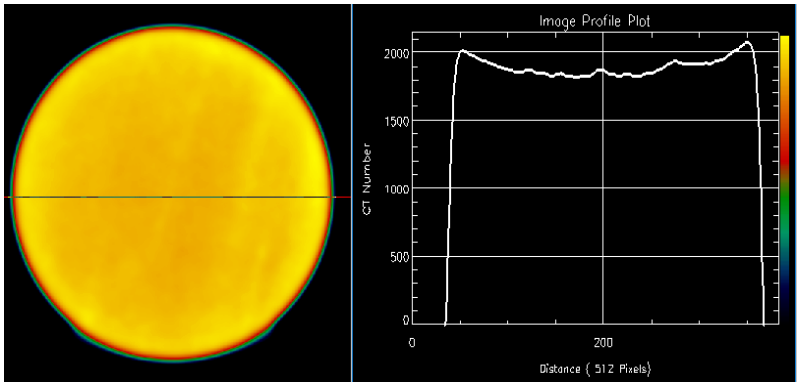
Slice	Average CT-number	Injected pore volume
	2000	initial
	1950	6 PVs
	1920	10 PVs

Table 18 CT-number of Bandera Core before and after Injecting 20 wt. % DTPA Combined with 3 wt. % K_2CO_3

Slice	Average CT-number	Injected pore volume
	2000	initial
	1870	6 PVs
	1820	10 PVs

6.4.4 Models to Predict Sand Production

Tixier et al., (1995) suggested a model that uses shear modulus to bulk compressibility ratio to expect sand production. The model was developed based on real data. Several wells have composition similar to Bandera sandstone. Khamehchi et al., (2015) validated Tixier's model to predict sanding problem using real field data. This model suggests that if the shear modulus to bulk compressibility is less than 0.8×10^{12} psi^2 (approximately 38 $\times 10^{18}$ Pa^2) sand problem will occur and high probability if the value was around. The main disadvantage of this method that the maximum rate at which sand production may happen cannot be estimated.

$$G = \frac{E}{2(1+\upsilon)} \tag{6.4}$$

$$C_b = \frac{3(1-2\upsilon)}{E} \tag{6.5}$$

Shear modulus to bulk compressibility ratio decreased for sandstone cores after injecting 6 pore volumes (**Figure 51**). Nevertheless, sand production is not expected for the treated Berea and Bandera samples because the ratio is higher than the threshold limit. Although sanding problem is not expected for this scenarios, other factors such as production rate and draw down should be considered. The applied model can only predict either sand problem will happen or not but cannot specify the effect of these factors. For instance, at very high production rate sand production will occur whether we reached shear modulus to bulk compressibility ratio limit or not. Moreover, water production may trig the sand production earlier.

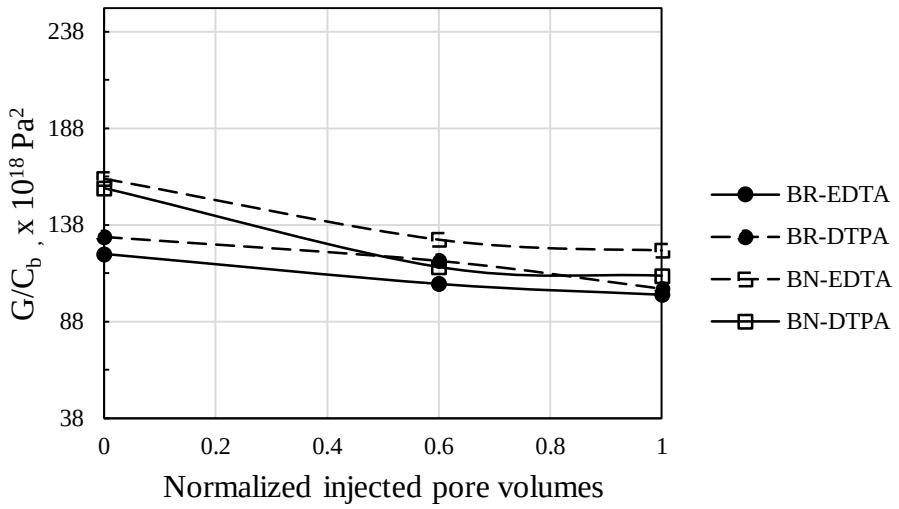


Figure 51 Predicting Sand Production Using Shear Modulus To Bulk Compressibility Ratio After Acidizing Berea And Bandera Cores Using EDTA And DTPA Solutions.

6.5 Conclusions

Rock mechanical properties was investigated after acidizing Berea and Bandera 2 inches cores using 20 wt. % of EDTA and DTPA at pH of 11 combined with 3 wt. % K_2CO_3 diluted using seawater at injection rate 5 cm^3/min and temperature 250^oF after injection up to 10 pore volumes .we can conclude that:

1. DTPA and EDTA solutions diluted using seawater enhanced the permeability ratio of Bandera and Berea sandstone cores.
2. The CT-scan measurement indicated no precipitations inside the cores.
3. Young's modulus and Shear modulus decreased as injected pore volume increased. Bandera samples showed the most significant reduction for both EDTA and DTPA solutions. In contrast, Berea samples did not show high drop in moduli values.
4. Slight increase was recorded in Poisson's ratio for Berea and Bandera.

5. Shear modulus in case of Bandera cores showed higher decrease than Berea cores. However, this reduction did not affect the rock integrity and no sand production was noticed.
6. Sand production is not expected at these conditions according to shear modulus to bulk compressibility ratio model.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

In this study, DTPA (diethylene tri-amine penta-acetic acid) diluted with deionized water and seawater combined with potassium carbonate was introduce to stimulate sandstone reservoirs.

Solubility tests showed that the optimum concentration of the chelating agents (HEDTA, EDTA and DTPA) was 20 wt. %. Adding 3 wt. % of potassium carbonate enriched the performance of the acids. No precipitation was noticed when seawater used to prepare the acids. DTPA showed the highest solubility with Bandera sandstone at 150^{o}F and pH of 11.

Berea and Bandera 2 inches length and 1.5 inches diameter acidized using chelating agents before and after adding the catalyst. The core flooding experiments conducted using 6 pore volumes of the acid by injection rate of 5 cm^3/min at 250^{o}F. 3 wt. % KCl used as brine to saturate and flush the cores. The new formulated acids found to be compatible with Berea and Bandera sandstone. It can be clearly seen that, the catalyst enhanced the performance of chelating agents when they prepared using deionized water or seawater. The permeability ratio improved by 36 % for Berea after adding the 3 wt. % of catalyst to 20 wt. % EDTA diluted using deionized water at pH of 11 and the injection

rate was 5 cm^3/min at temperature 250°F. While the ratio was around 40 % for DTPA. For Bandera diluting the acids with seawater showed the best enhancement in permeability ratio. 27 % was recorded for 20 wt. % EDTA and 40 % for DTPA. ICP analysis showed that adding 3 wt. % of potassium carbonate to DTPA and EDTA increased the chelated amount of calcium, magnesium and ferric cations.

Decreasing the injection rate to 1 cm^3/min provides more contact time between the acid and rock which raised the amount of chelated ions. Decreasing the injection rate increased the permeability ratio to more than double for Berea and 70 % for Bandera using DTPA diluted using seawater with 3 wt. % of catalyst. In case of EDTA the ratio was 76 % for Berea and 45 % for Bandera.

The new formulated acid worked better at 250°F thus decreasing the temperature to 150°F reduced its efficiency. Decreasing the temperature minimize the reaction rate. For DTPA the percent decreased to 15 % for Berea and 10 % for Bandera. The same decrease was noticed for EDTA, 7 % for Berea and 11 % for Bandera.

Rock mechanical results showed the effect of injected pore volume of the acid on the rock integrity. Reduction in Young's modulus values when the injected pore volume increased indicates success of the treatment. Bandera cores acidized with 20 wt. % DTPA combined with 3 wt.% potassium carbonate diluted using seawater showed the largest decrease in Young's modulus value as well as highest permeability enhancement after injecting 10 PVs. Berea samples showed insignificant change in elastic moduli values. Young's modulus decreased as injected pore volume increased. Bandera samples showed

the most significant reduction for both EDTA and DTPA solutions around 15 %. In contrast, Berea samples did not show high drop in Young's modulus ratio.

We can conclude that according to shear modulus to bulk compressibility ratio sand production is not expected to happen. However, factors such as production rate, draw dawn and water cut should be considered during well production to avoid early sanding.

7.2 Recommendations

1. Study of reaction kinetics of seawater based chelating agent with sandstones before and after adding the catalyst.
2. Destructive methods such as tri-axial and tensile strength are recommended to be used to address the effect of using the new formulated fluids on the rock integrity of sandstone cores.

REFERENCES

[1] Al-Dahlan, M. N., Al-Harbi, B. G., & Al-Khaldi, M. H. 2013. Evaluation of Chelating-Hydrofluoric Systems. Paper IPTC 16969 presented at International Petroleum Technology Conference held in Beijing, china, 6-28 March.

[2] Al-Anazi, H.A., Nasr-El-Din, H.A., Hashem, M.K., and Hopkins, J.K. 2000. Matrix Acidizing of Water Injectors in a Sandstone Field in Saudi Arabia: A Case Study. Paper SPE 62825 presented at the SPE/AAPG Western Regional Meeting, California, 19-23 June.

[3] Al-Harbi, B. G., Al-Dahlan, M. N., Al-Khaldi, M. H., Al-Harith, A.M., and Abadi, A.K. 2013.Evaluation of organic-hydrofluoric acid mixtures for sandstone acidizing. Paper IPTC 16976 presented at International Petroleum Technical Conference held in Beijing, China 26-28 March.

[4] Al-Harbi, B. G., Al-Dahlan, M. N., Al-Khaldi, M.H. 2012. Aluminum and Iron Precipitation During Sandstone Acidizing Organic-HF Acids. Paper SPE 151781 presented at the SPE International Symposium and Exhibition on Formation Damage Control held in Lafayette, Louisiana, USA, 15-17 February.

[5] Al-Harbi, B.G., Al-Khaldi, M.H., Al-Dossary, K.A. 2011. Interaction of Organic-HF systems with Aluminosilicate: Lab experience and field recommendations. Paper SPE 144100 presented at the SPE European Formation Damage Conference and Exhibition held in Noordwijk, the Netherlands 7-10 June.

[6] Ali, A.H.A., Frenier, W.W., Xiao, Z. and Ziauddin, M. 2002. Chelating Agent-Based Fluids for Optimal Stimulation of High-Temperature Wells. Paper SPE 77366 presented at the SPE Annual Technical Conference and Exhibition held in San Antonio, Texas, 29 September–2 October.

[7] Al-Shaalan, T.M. and Nasr-EI-Din, H.A.2000. Mathematical Modeling of Sandstone Stimulation: A Critical Review of Available Models. Paper SPE 00443 presented at NACE International Conference held in Houston, Texas, USA 1 January.

[8] Civan, F. 2007. *Reservoir Formation Damage: Fundamentals, Modeling, Assessment and Mitigation.* Houston, Texas: Gulf Publishing Company.

[9] Clegg, J. D.2007. *Petroleum Engineering Handbook, Volume IV: Production Operations Engineering.* Society of Petroleum Engineers, Richardson, TX.

[10] Crocker, M.E., Donaldson, E.C., and Marchin, L.M. 1983.Comparison and Analysis of Reservoir Rocks and Related Clays. Paper SPE 11973 presented at the 58th Annual Technical Conference and Exhibition held in San Francisco, USA, 5-8 October.

[11] De Wolf, C. A., Bang, E., Bouwman, A., Braun, W., De Oliveira, E., & Nasr-El-Din, H.A.2014. Evaluation of Environmentally Friendly Chelating Agents for Application in Oil and Gas Industry. Paper SPE 168145 presented at the International Symposium and Exhibition on Formation Damage Control held in Lafayette, Louisiana, USA, 26-28 February.

[12] Economides, M. J., Hill, A. D., Ehlig-Economides, C. and Zhu, D. 2012. *Petroleum Production Systems,* 2nd edition, Prentice Hall.

[13] Fjar, E., Holt, R. M., Raaen, A., Risnes, R., and Horsrud, P. 2012. *Petroleum related rock mechanics*, Elsevier.

[14] Fernier, W.W., Wilson, D., Crump, D. and Jones, L.2000. Use of Highly Acid-Soluble Chelating Agents in Well Stimulation Services. Paper SPE 63242 presented at SPE Annual Technical Conference and Exhibition held in Dallas, Texas, USA, 1-4 October.

[15] Fredd, C.N., Fogler, H.S. 1997. Chelating Agents as Effective Matrix Stimulation Fluids for carbonate Formations. Paper SPE 37212 presented at the SPE International Symposium on Oil Field Chemistry held in Houston, Texas, USA 18-21 February.

[16] Frenier, W.W., Rainey, M., Wilson, D., Cruom, D. and Jones, L. 2003. A Biodegradable Chelating agent is developed for Stimulation of Oil and Gas Formations. Paper SPE 80597 presented at SPE/EPA/DOE Exploration and Production Environmental Conference held in San Antonio, Texas, USA, 10-12 March.

[17] Frenier, W. W., Fredd, C. N., & Chang, F. 2001. Hydroxyaminocarboxylic Acids Produce Superior Formulations for Matrix Stimulation of Carbonates. Paper SPE 68924 presented at SPE European Formation Damage Conference, The Hague, Netherlands, 21-22 May.

[18] Gdanski, R. 1997. Kinetics of the Primary Reaction of HF on Alumino-Silicate. Paper SPE 37459 presented at SPE Production Operations Symposium held in Oklahoma City, USA, 9-11 March.

[19] Guo, B., Lyons, W.C., Ghalambor, A. 2011. *Petroleum Production Engineering, A Computer-Assisted Approach*. Gulf Professional Publishing.

[20] He, J., Mohamed, I. M., & Nasr-El-Din, H. A. (2011). Mixing Hydrochloric Acid and Seawater for Matrix Acidizing: Is It a Good Practice?. Paper SPE 143855 presented SPE European Formation Damage Conference held in Noordwijk, The Netherlands, 7-10 June.

[21] Himes, R. E., Vinson, E. F., & Simon, D. E. 1991. Clay Stabilization in Low-Permeability Formations. SPE Production Engineering **6**(3): 252 – 258.

[22] Jaramillo, O.J., Romero, R., Ortega, A., Milne, A., Lastre, M. 2010. Matrix Acid Systems for Formations with High Clay Content. Paper SPE 126719 presented at the SPE International Symposium and Exhibition on Formation Damage Control held in Lafayette, Louisiana, USA, 10-12 February.

[23] Ji, Q., Zhou, L., Nasr-El-Din, H.A. 2014.Acidizing Sandstone Reservoirs Using Fine Control Acids. Paper SPE 169395 presented at the SPE Latin American and Caribbean Petroleum Engineering Conference held in Maracaibo, Venezuela, 21-23 May.

[24] Khamehchi, E., Reisi, E. 2015. Sand production prediction using ratio of shear modulus to bulk compressibility (case study). *Egyptian Journal of Petroleum* **24**(2):113–118.

[25] Kunze, K. R., & Shaughnessy, C. M. 1983. Acidizing Sandstone Formations With Fluoboric Acid. Paper SPE 9387 presented at the SPE Annual Technical Conference and Exhibition held in Dallas 21-24 September.

[26] Labrid, J.C. 1975. Thermodynamic and Kinetic Aspects of Argillaceous Sandstone Acidizing. *SPEJ* **15** (2): 117-128.

[27] Mahmoud, M. A. 2014. Evaluating the Damage Caused by Calcium Sulfate Scale Precipitation During Low- and High-Salinity-Water Injection. *Journal of Canadian Petroleum Technology* **53**(3): 141 – 150.

[28] Mahmoud, M. A., Nasr-El-Din, H. A., De Wolf, C., & Alex, A. (2011a). Sandstone Acidizing Using A New Class of Chelating Agents. Paper SPE

139815 presented at the SPE international symposium on Oil field chemistry held in Woodlands, Texas, USA 11-13 April.

[29] Mahmoud, M. A., Nasr-El-Din, H. A., De Wolf, C., & LePage, J. N. (2010). Stimulation of Carbonate Reservoirs Using GLDA (Chelating Agent) Solutions. Paper SPE 132268 presented at Trinidad and Tobago Energy Resources Conference held in Port of Spain, Trinidad, 27-30 June.

[30] Mahmoud, M. A., Nasr-El-Din, H. A., De Wolf, C., LePage, J., & Bemelaar, J. (2011b). Evaluation of a New Environmentally Friendly Chelating Agent for High-Temperature Applications. *SPE Journal* **16** (3): 559 – 574.

[31] Mahmoud, M.A. and Nasr-El-Din, H.A. (2011c). Novel Environmentally Friendly Fluids to Remove Carbonate Minerals from Deep Sandstone Formations. Paper SPE 143301 presented at the SPE European Formation Damage Conference, Noordwijk, The Netherlands, 7–10 June.

[32] Mahmoud, M.A., Nasr-El-Din, H.A. & De wolf, C. A. (2015). High-Temperature Laboratory Testing of Illitic Sandstone Outcrop Cores With HCl-Alternative Fluids. *SPE Production & Operations.* **30** (01):43-51.

[33] Mostofizadeh, B., & Economides, M. J. (1994). Optimum Injection Rate From Radial Acidizing Experiments. Paper SPE 28547 presented at SPE Annual Technical Conference and Exhibition held in New Orleans, Louisiana, 25-28 September.

[34] Mcleod, H.O, Jr. and Norman, W.D. Sandstone Acidizing. 2000. Ch 18 in *Reservoir stimulation*, 3 rd edition, Economides, M.J., and Nolte, K.G., John Wiley and Sons, Chichester, UK.

[35] McLeod, H.O. 1984. Matrix Acidizing. *Journal of Petroleum Technology* **36**(12):2055-2069.

[36] Nasr-El-Din, H.A., Dana, H., Tomos, V., Stanitzik, T., De Wolf, C.A. and Alex, A. 2014. Field Treatment to Stimulate an Oil Well in an Offshore Sandstone Reservoir Using a Novel, Low Corrosive, Environmentally Friendly Fluid. Paper SPE 168163 presented at the SPE International Symposium and Exhibition on Formation Damage Control held in Lafayette, Louisiana, USA, 26-28 February.

[37] Oddo, J. E., Smith, J. P., & Tomson, M. B. (1991). Analysis of and Solutions to the $CaCO_3$ and $CaSO_4$ Scaling Problems Encountered in Wells Offshore Indonesia. Paper SPE 22782 presented at SPE Annual Technical Conference and Exhibition held in Dallas, Texas, 6-9 October.

[38] Parkinson, M., Munk, T., Brookley, J., Caetano, A., Albuquerque, M., Cohen, D., and Reekie, M. 2010. Stimulation of Multilayered-Carbonate-Content Sandstone Formations in West Africa Using Chelant-Based Fluids and Mechanical Diversion. Paper SPE 128043 presented at the SPE International Symposium and Exhibition on Formation Damage, Lafayette, Louisiana 10-12 February.

[39] Scheuerman, R. F. 1988. A Buffer-Regulated HF Acid for Sandstone Acidizing to 550 degrees F. Society of Petroleum Engineers. *SPE Production Engineering journal* **3(**01):15 – 21

[40] Shafiq, M.U., Shuker, M.T. 2013. Finding Suitable Acid for Acidizing Of Low Permeable Sandstone Formation: A Research. Paper SPE 169641 presented at SPE/PAPG Annual Technical Conference held in Islamabad, Pakistan 26-27 November.

[41] Simon, D.E. and Anderson, M.S.1990. Stability of Clay Minerals in Acid. Paper SPE 19422 presented at SPE Formation Damage Control Symposium held in Lafayette, Louisiana, USA 22-23 February.

[42] Smith, M.J, and Clark, G.J., Hendrickson, A.R., and Egbogah E.O. 1986.Acidization of Dirty Sandstones with Buffered HF Acid Systems. Paper SPE 14826 presented at the Seventh SPE Symposium on Formation Damage Control of the Society of Petroleum Engineers held in Lafayette, Louisiana, USA 26-27 February.

[43] Sokhanvarian, V., Nasr-El-Din, H.A., Wang, G. and De Wolf, C. A. 2012. Thermal Stability Of Various Chelates That Are Used In The Oilfield And Potential Damage Due To Their Decomposition Products. Paper SPE 157426 presented at the SPE international Production and Operations Conference and Exhibition held in Doha, Qatar, 14-16 May.

[44] Tixier, M. P., Loveless, G. W., & Anderson, R. A. (1975, March 1). Estimation of Formation Strength From the Mechanical-Properties Log. *Journal of Petroleum Technology* **27**(03): 283 – 293.

[45] Thomas, R.L., Nasr-El-Din, H.A., Lynn, J.D., Mehta, S., and Zaidi, S.R. 2001. Precipitation During the Acidizing of a HT/HP Illitic Sandstone Reservoir in Eastern Saudi Arabia: A Laboratory Study. Paper SPE 71690 presented at the SPE ATCE, New Orleans, Louisiana, 30 September-3October.

[46] Yang, F., Nasr-El-Din, H. A. and AL-Harbi, B., 2012. Acidizing Sandstone Reservoirs Using HF and Formic Acids. Paper SPE 150899 presented at the SPE International Symposium and Exhibition on Formation Damage Control held in Lafayette, Louisiana, USA, 15-17 February.

[47] Zhou, L., Nasr-El-Din, H.A., 2013. Acidizing Sandstone Formations Using a Sandstone Acid System for High Temperature. Paper SPE 165084 presented at the SPE European Formation Damage Conference and Exhibition held in Noordwijk, the Netherlands 5-7 June.

Appendix

Table 19 Properties of Berea and Bandera Cores Treated by 6 PVs of EDTA Solutions (at pH of 11) Diluted Using Deionized Water and Seawater at Injection Rate of 5 cm^3/min and Temperature of 250ºF.

Sample number	Injected Volume, cm^3	L , in	$Ø_i$, %	$K_{initial}$, mD	K_{final} , mD	Acid type
BR1	63	1.95	18.6	86.87	100.32	E20C3-sea
BR2	56.7	1.9	17.18	101.1	108.05	E20-sea
BR3	60.12	2	17.3	105.6	133.2	E20-DI
BR4	67.7	2	19.5	92.81	126.12	E20C3-DI
BN1	55.66	1.85	17.28	8.2	10.5	E20C3-sea
BN2	59.86	2	17.8	9.31	10.4	E20-sea
BN3	10.25	2	17.71	8.760	9.24	E20-DI
BN4	61.7	2	17.76	8.1	9.55	E20C3-DI

Table 20 Properties of Berea and Bandera Cores Treated by 6 PVs of DTPA Solutions (at pH of 11) Diluted Using Deionized Water and Seawater at Injection Rate of 5 cm^3/min and Temperature of 250ºF.

Sample number	Injected Volume, cm^3	L , in	$Ø_i$, %	$K_{initial}$, mD	K_{final} , mD	Acid type
BR5	64.4	2	18.53	88.22	108.77	D20C3-sea
BR6	66.9	2	19.24	97.4	118.62	D20-sea
BR7	63	2	17.61	83.60	109.4	D20-DI
BR8	64.32	1.9	19.5	96.82	134.44	D20C3-DI
BN5	66.87	2.05	18.85	8.7	12.2	D20C3-sea
BN6	58.4	1.86	18	7	9	D20-sea
BN7	57.64	1.95	17.03	8.75	11	D20-DI
BN8	61.8	2	17.3	9	12	D20C3-DI

Table 21 Properties of Berea and Bandera Cores Treated by 6 PVs of EDTA and DTPA Solutions (at pH of 11) Diluted Using Seawater Combined with 3 wt. % K_2CO_3 and Injection Rate of 1 cm^3/min and Temperature of 250ºF.

Sample number	Injected Volume, cm^3	L , in	$Ø_i$, %	$K_{initial}$, mD	K_{final} , mD	Acid type
BN9	56.71	1.9	17.18	8.68	12.57	E20C3-sea
BR9	70.8	2	20.39	85.67	151.08	E20C3-sea
BR10	60.84	2	17.5	100	226	D20C3-sea
BN10	57.66	2	17.03	8.27	14	D20C3-sea

Table 22 Properties of Berea and Bandera cores treated by 6 PVs of EDTA and DTPA solutions (at pH of 11) Diluted Using Seawater Combined with 3 wt. % K_2CO_3 and Injection Rate of 5 cm^3/min and Temperature of 150ºF.

Sample number	Injected Volume, cm^3	L , in	$Ø_i$, %	$K_{initial}$, mD	K_{final} , mD	Acid type
BN11	62.58	1.8	17.41	7.13	7.93	E20C3-sea
BR11	66.1	2.1	18.12	90.1	96	E20C3-sea
BN12	61.52	2	17.71	7.44	8.13	D20C3-sea
BR12	66.9	2	19.21	100.33	115.8	D20C3-sea

Table 23 Properties of Berea and Bandera Cores (6 Inches Length) Treated by 6 PVs of EDTA and DTPA Solutions (at pH of 11) Diluted Using Seawater Combined with 3 wt. % K_2CO_3 and Injection Rate of 5 cm^3/min and Temperature of 250ºF.

Sample number	Injected Volume, cm^3	L , in	$Ø_i$, %	$K_{initial}$, mD	K_{final} , mD	Acid type
BN13	188.6	6	18.1	8.47	10.9	D20C3-sea
BR13	178.8	5.7	18	92	113.3	D20C3-sea
BN14	181.8	6	17.4	8.56	10.4	E20C3-sea
BR14	181.3	6	17.1	97	112	E20C3-sea

Vitae

Name	: Ahmed Abdulazeem Ahmed Hamza.
Nationality	: Sudanese.
Date of Birth	: 8/October/1989
Email	: ahmedalkasir.09@gmail.com.
Address	: Block 4-UMBADDA-Omdurman-Sudan
Academic Background	: B.Sc. in Petroleum Engineering, (2011) Department of Petroleum and Natural Gas Engineering Faculty of Engineering, University of Khartoum Khartoum, Sudan.
Published Papers	: **A. Abdulazeem**, S. Alnuaim. 2016. New Method to Estimate IPR for Fishbone Oil Multilateral Wells in Solution Gas Drive Reservoirs. Paper SPE-KSA-136 presented at the Annual Technical Symposium and Exhibition held in Dammam, Saudi Arabia, 25–28 April.